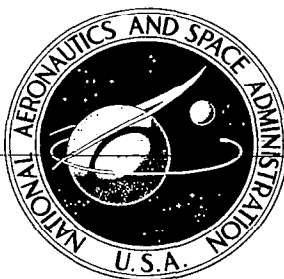


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SILVER-CADMIUM BATTERY DEVELOPMENT PROGRAM

by James M. Rice

Prepared under Contract No. NAS5-1431 by
TELECOMPUTING CORPORATION
Denver, Colo.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1964



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ABSTRACT

The development of a lightweight, silver-cadmium secondary battery for space applications is described in the following report. The original concept for the battery incorporated the use of unit cells, with units connected in series to provide sufficient voltage, and cells connected in parallel to provide sufficient capacity. The electrodes were to be of the duplex type, and the battery case was to be filament-wound, for light weight, utilizing the circular cells as a mandrel.

A change in the concept was required during the program. The cells were encased in plastic cell containers and the duplex electrode concept could not be realized. The filament-wound case was maintained.

In spite of many difficulties, the objective of the program--development of a lightweight battery with long cycle life--was achieved.

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SUMMARY

NASA SILVER-CADMIUM BATTERY RESEARCH PROGRAM

OBJECTIVES VERSUS ACCOMPLISHMENTS

Parameter	Objective	Actual
Nominal Voltage Duty Cycle Capacity	12 Volts 5 amps - 40 minutes Charge - 60 minutes	12 Volts 4 amps - 35 minutes Charge - 55 minutes a. Cell formation qualifying re- quirement = 200 AM b. Battery capacity after 357 cycles = 300 AM
Cycle Life	5000 Cycles (not to be tested)	a. Single cell = 1800 cycles b. Prototype group = 500 cycles c. Battery = 357 cycles (testing discontinued)
Temperature Range	32°F to 122°F	a. Cell: -40°F to 150°F b. Battery: 5°F to 113°F
Weight	Five pounds	3.6 pounds
Volume	60 cubic inches	55 cubic inches ex- cluding connector
Weight Loss Through Case	1.5 gms/24 hrs/m ²	0.58 gms/24 hrs/m ²
Case Design Pressure	150 psig	550 psig

PHASE I

I. INTRODUCTION

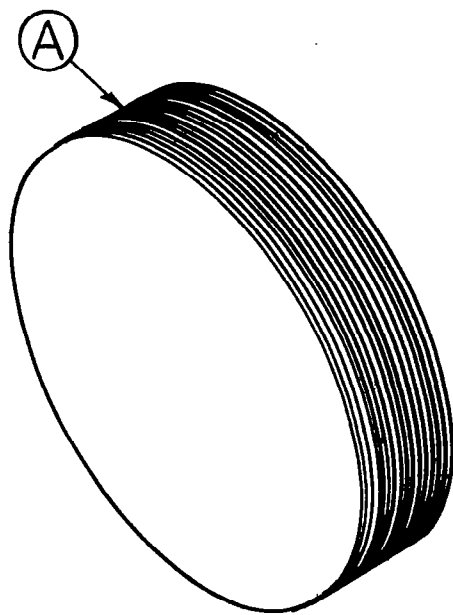
A. Objective

The objective of this program was the advancement of the state-of-the-art of secondary electrochemical power sources. By the development of new concepts of structural and electrochemical design, a reliable, lightweight, high efficiency, silver-cadmium battery system, capable of operating over a very long cycle life in a space environment, was developed.

B. Initial Concept

Initially it was proposed that the battery case consist of a cylinder with a length several times its diameter. The cylinder wall would be filament wound, using glass fiber reinforcement. The end closures were to be a molded glass flake-reinforced organic resin composite, either bonded to the cylinder or attached integrally during the winding process. The mandrel for winding the case was to be the battery materials, suitably enclosed in a preliminary casing designed to maintain electrode alignment and electrolyte. The details of this design are illustrated in Figures 1, 2 and 3. The following comments on the illustrations provide a clear picture of the initial design concept.

1. The battery is made up of unit cells, each unit containing sufficient electrodes, connected in series, to provide
a about 12.5 volts (probably 12 electrodes). Sufficient unit cells are connected in parallel to provide one specified capacity.
2. The battery electrodes are of the duplex type; that is, a foil current collector with the cadmium active material on one side and the silver active material on the other side.
3. The electrodes -- circular in shape -- are assembled by stacking with thin rubber or other polymer ring seals interposed between them. These seals serve as spacers which assure the proper separation of electrodes, and provide a cavity between electrodes for semipermeable



Unit Cell Detail

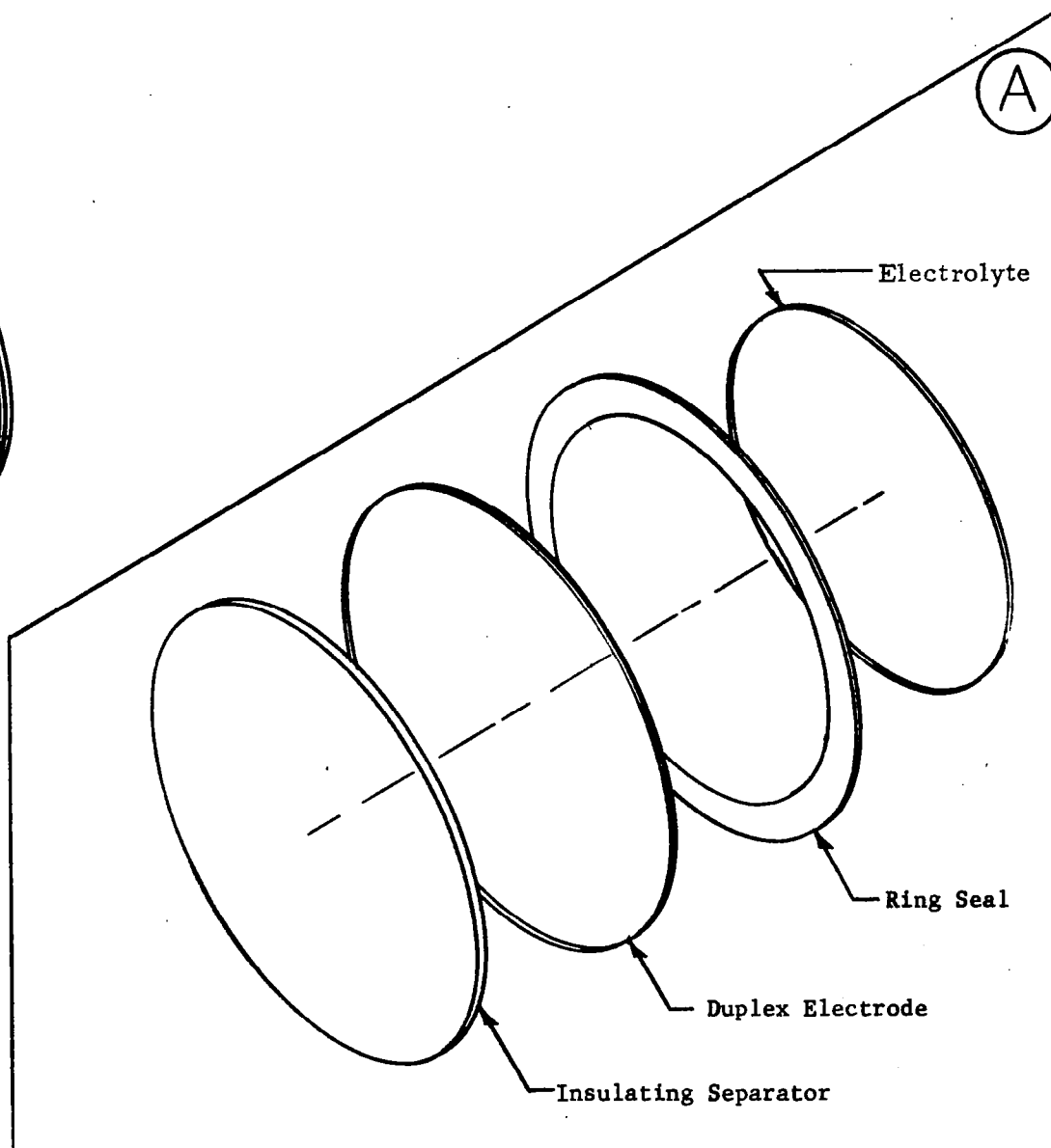


Figure 1. Unit Cell Detail

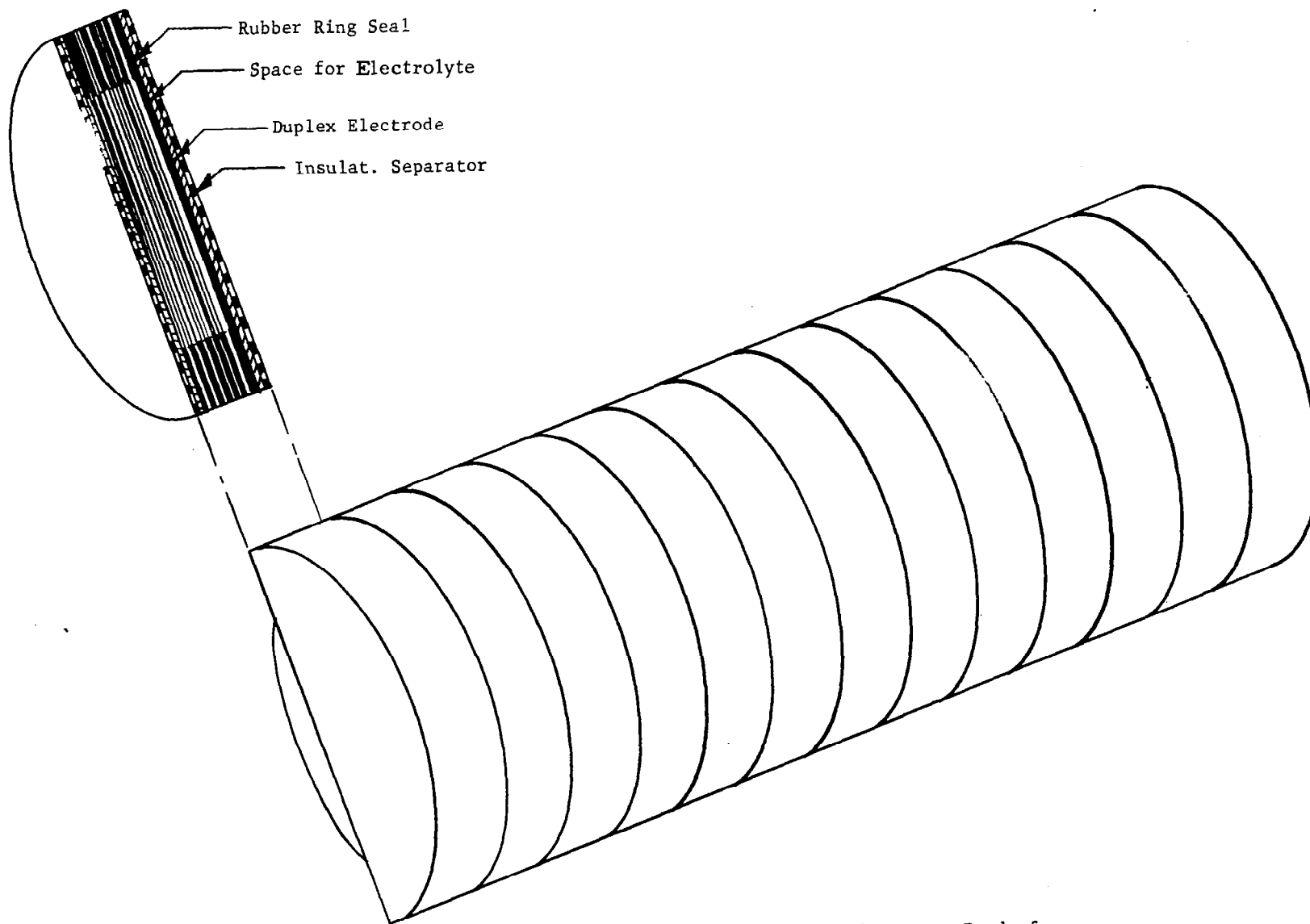


Figure 2. Completed Battery Ready for
Filament Winding

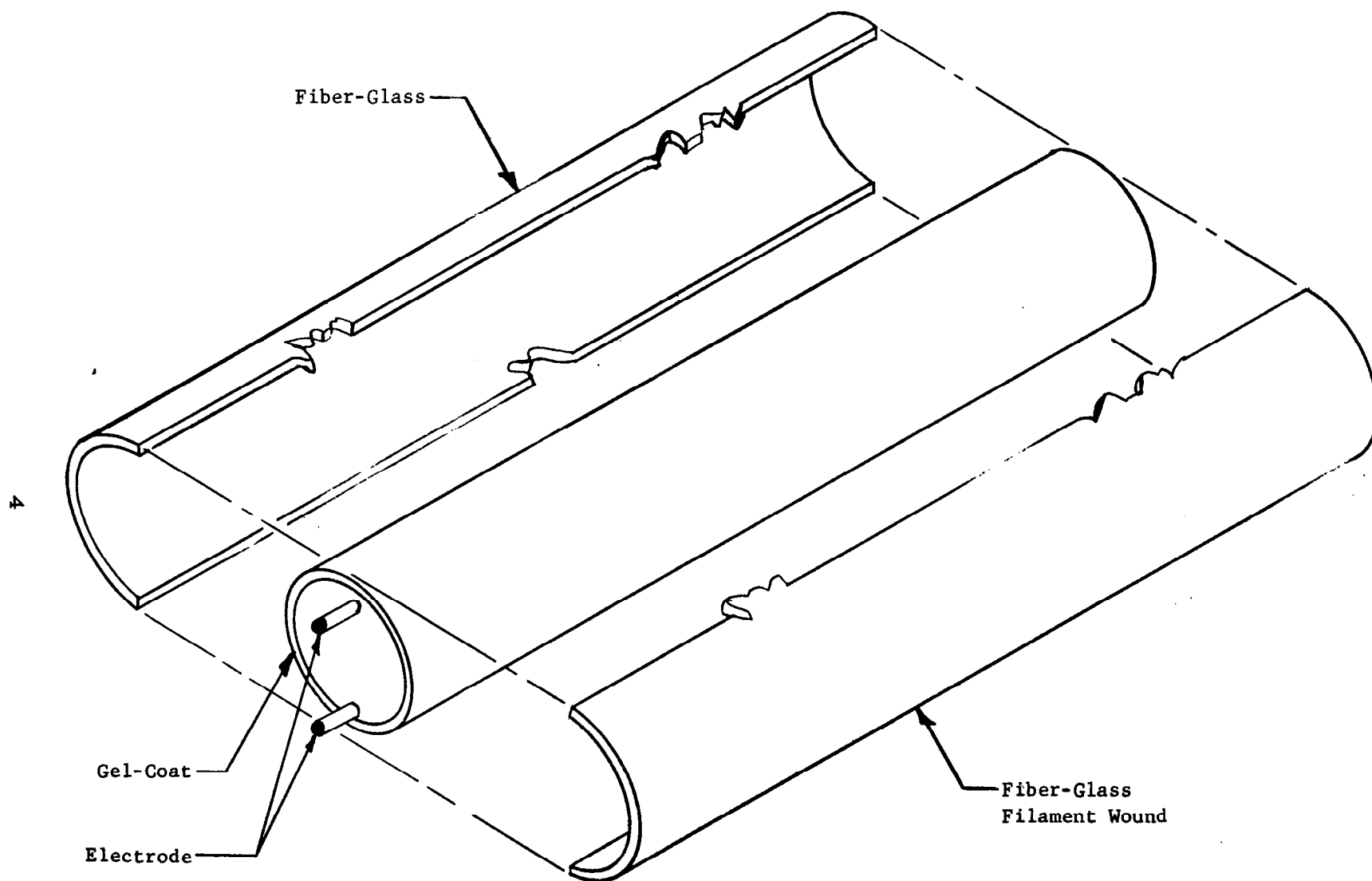


Figure 3. Battery Case Assembly

membrane separators and electrolyte. The ring seals are adhesive bonded to the electrodes, and provide the initial seal against gas or liquid leakage.

4. At the two ends of the cell, special electrodes are used which have active material on only one side of the foil current collector. These electrodes seal the ends of the unit cell, and are structurally reinforced with flake-reinforced resin composite flat laminates of glass material. These laminates serve as insulators, and also provide sufficient stiffness to maintain the proper alignment of the electrodes in the unit cell.
5. The electrolyte is injected into each cell by inserting a hypodermic needle through the ring seal.
6. The resulting unit cell is electrochemically operative at this stage, but incomplete, since it will not be capable of full performance in terms of leakage, resistance to internal pressure and to "g" forces.
7. Sufficient unit cells to provide the desired capacity are stacked end-to-end and bonded together, thus forming the mandrel for the filament winding process. Prior to the winding operation, a resin gel coat is applied to the outer surface of the battery. This coating serves as an additional seal against leakage, and also assures no contact between glass fibers and electrolyte. This is necessary, because the presence of silicate in the electrolyte is harmful.
8. Additional layers of glass flake containing organic films are added as necessary to provide the desired gas and liquid impermeability.
9. The electrical leads from the terminal electrodes of each cell are brought through the gel coat, and positioned so that the filament winding operation will fix the collectors in place, and also provide additional sealing capability.
10. The final step consists of filament winding the entire case, using the gel coated unit cells as the mandrel. The end closures are flat plates with turned over edges, which are wound in during the winding operation. The parallel leads from each unit cell consist of metal foil strips wound into the wall of the battery and terminating at one end.

C. Final Concept

During a meeting held at Power Sources on 14 March 1962, it was disclosed that the concept of the cell design had to be changed because the original concept of the duplex plates, gas elimination, and ion exchange could not be realized within the scope of this contract. The Power Sources Division therefore suggested a more conventional design of the battery cells, however, maintaining the weight advantages of a filament wound shell. The design approach of the cell, the battery, the location of the leads and the requirements associated with winding were discussed with the Power Sources personnel and it was decided that NARMCO would determine the optimum material for the new cell-container as a part of the Phase I effort. It was also suggested that NARMCO would manufacture the cell containers for Power Sources. Figure 4 illustrates the revised concept for the battery. Narmco drawing 5317B (Appendix A) illustrates the final design of the Battery Terminal Assembly.

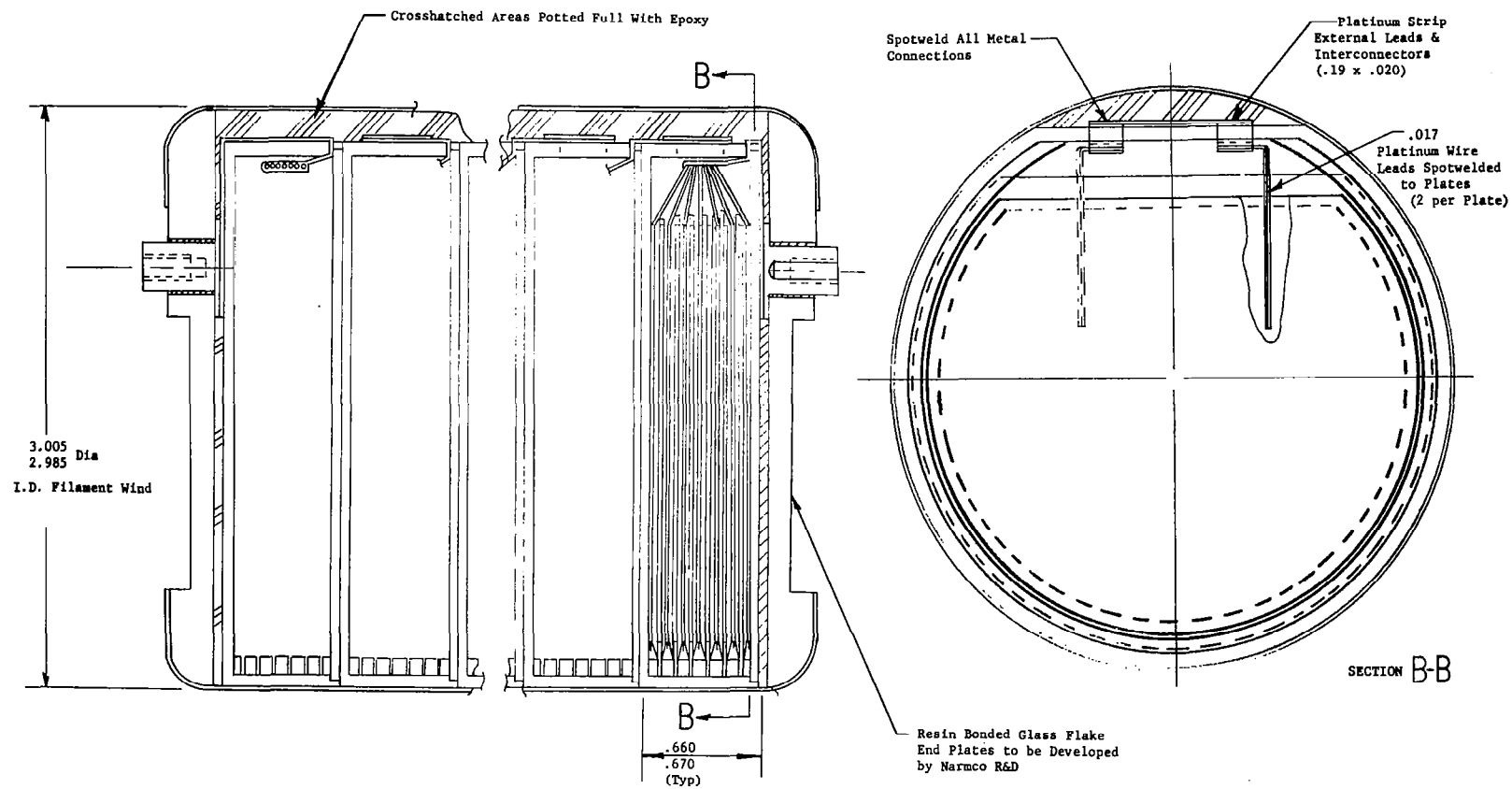


Figure 4. Layout - NASA, Experimental Cell

II. DISCUSSION

A. Ring Seal Development

This study was initiated to determine the suitability of various elastomeric compositions to position the electrodes and provide a sealed cavity for the electrolyte in a silver-cadmium battery of the initial design concept. It also served to determine preferred techniques for bonding the elastomeric seal to the electrodes and to the membrane.

1. Evaluation of various elastomers

For the elastomeric seal to perform adequately, it must not be significantly deteriorated by continuous contact with 30% aqueous KOH solution (the electrolyte) held at 100°F. In other words, the rubber seal should not swell in the KOH solution or otherwise change dimensions, nor should it be attacked by the caustic solution and either change weight or decrease appreciably in strength.

It is also obvious that the rubber seal must be impermeable to the 30% aqueous KOH solution. In addition, the seal must be self-sealing to prevent electrolyte leakage after the injection of the KOH solution into the small cells by means of a hypodermic needle.

Eight various types of elastomers were tested. The materials were compounded and molded into flat sheets about 0.080 x 6.0 x 6.0 inches. From these molded sheets, half-inch wide "dog-bone" tensile strength test specimens were cut.

The initial tensile strength and elongation values of these eight type elastomers were obtained. Tensile strength and elongation values were then determined after seven days' soaking in 30% KOH solution maintained at a temperature of 100°F. Thirty-day soak results were also obtained on the first four materials. The eight elastomers that were screened are characterized as follows:

Enjay 035, a butyl rubber
Hycar 1042, a nitrile rubber
Cis-4, a polybutadiene rubber (two formulations)
Shell's S-1509, a styrene-butadiene rubber
Hycar 2001, a high styrene butadiene rubber
Shell's 305WP, a polyisoprene rubber
Du Pont's Adiprene C, a urethane elastomer

The last four were selected because of their known favorable resistance to highly alkaline conditions and to H₂O. Results of these tests are shown in Table I.

Because of the very high elongation of Shell's 305WP, Adiprene C, and the Cis 4 elastomers, some difficulty was experienced in obtaining reliable elongation values with the testing equipment available. In many instances the gage length was shortened to .25" to 1" instead of the standard 2". This procedure gave reasonable tensile strength values, but the percent elongation was increased significantly as the gage length was reduced. With the same composition, for example, the percent elongation would nearly double as the gage length was reduced to 1" from the standard 2".

Having to change the gage length made it difficult to determine the true effect of the KOH soak on the elongation of the elastomeric compositions.

To observe dimensional and weight changes, the thickness width, and weight of the "dog-bone" were determined initially and after 7 and 30 days soaking in 30% KOH solution held at 100°F. The results obtained are shown in Tables II, III and IV.

2. Silver electrode bonding study

a. Bonding of silver foil to itself

Studies were conducted in order to learn of any problems associated with the silver in obtaining good bonds to the elastomer. Metlbond 3135 adhesive was used to prepare 1/8" overlap bonds with 0.5" x 0.002" x 1.5" and 0.5" x 0.003" x 1.5" strips of silver foil at a pressure of 5 psi.

TABLE I

CHANGES OF MATERIAL PROPERTIES

Type Elastomer	Before Soaking		After 7 Days Soaking*			After 30 Days Soaking*		
	Tensile Strength psi	Elongation %	Tensile Strength psi	Elongation %	% Change in Original Tensile Strength	Tensile Strength psi	Elongation psi	% Change in Original Tensile Strength
Enjay 035	774	375	713	258	- 7.9	807	275	+ 4.27
Hycar 1042	1346	144	1178	143	-12.5	1386	250	+ 2.97
Cis-4 Formulation A	575	715	449	325	-21.9	415	716	-27.8
Cis-4 Formulation B	591**	1113	-	-	-	554	1239	- 6.25
Shell's S-1509	753	314	741	609	-1.59	-	-	-
Hycar 2001	1559	246	1328	367	-14.8	-	-	-
Adiprene C	951	814	1033	1900***	+ 8.6	-	-	-
Shell's 305WP	1153	634	1432	1693***	+24.2	-	-	-

* At 100°F in 30% KOH solution.

** Only approximate since had too much elongation to break within the limits of the Instron testing machine.

*** To break these elastomers a very short gauge length was used, thus making these elongation values meaningless.

TABLE II
CHANGES OF DIMENSIONS AND WEIGHT

Elastomeric Compositions	Before Soaking			After 7 Days Soaking*		
	Thickness	Width	Weight	Thickness	Width	Weight
<u>Enjay 035</u>						
Specimen No.						
1	0.088	0.511	6.6563	0.088	0.512	6.6720
2	0.084	0.513	6.4654	0.085	0.511	6.4715
3	0.077	0.514	-	0.078	0.513	-
4	0.084	0.514	-	0.084	0.513	-
<u>Hycar 1042</u>						
Specimen No.						
A	0.079	0.515	6.7807	0.079	0.514	6.7795
B	0.079	0.510	6.7780	0.079	0.509	6.7767
C	0.079	0.513	-	0.079	0.510	-
D	0.079	0.513	-	0.079	0.509	-
E	0.080	0.512	-	0.080	0.509	-
<u>Cis-4 Formulation A</u>						
Specimen No.						
1A	0.081	0.516	6.0323	0.081	0.515	6.0307
2A	0.083	0.512	6.1176	0.083	0.512	6.1206
3A	0.083	0.516	-	0.083	0.514	-
4A	0.082	0.516	-	0.080	0.515	-
<u>Cis-4 Formulation B</u>						
Specimen No.						
1B	0.083	0.517	6.2577	0.084	0.517	6.2594
2B	0.085	0.515	6.3590	0.084	0.516	6.3603
3B	0.086	0.515	-	0.085	0.516	-
4B	0.088	0.517	-	0.086	0.515	-

* At 100°F in 30% KOH solution

TABLE III
CHANGES OF DIMENSIONS AND WEIGHT

	Before Soaking			After 30 Days Soaking*		
	Thickness Inches	Width Inches	Weight Grams	Thickness Inches	Width Inches	Weight Grams
Enjay 035 Specimen No.						
5	0.077	0.513	5.7263	0.078	0.513	5.7576
6	0.077	0.511	5.7251	0.078	0.513	5.7695
7	0.078	0.512	-	0.079	0.514	-
8	0.083	0.514	-	0.083	0.512	-
Hycar 1042 Specimen No.						
F	0.079	0.511	6.7787	0.078	0.510	6.7772
G	0.079	0.512	6.6872	0.078	-	6.6859
H	0.078	0.511	-	0.078	-	-
I	0.080	0.511	-	0.080	-	-
J	0.078	0.511	-	0.078	-	-
Cis-4 Formulation A Specimen No.						
5A	0.083	0.518	6.0193	0.082	0.518	6.0272
6A	0.085	0.520	6.0530	0.082	0.516	6.0637
7A	0.079	0.510	-	0.079	0.515	-
8A	0.082	0.511	-	0.081	0.516	-
Cis-4 Formulation B Specimen No.						
5B	0.086	0.516	6.3725	0.083	0.503	6.3906
6B	0.085	0.503	6.1059	0.082	0.505	6.1190
7B	0.087	0.505	-	0.085	0.513	-
8B	0.085	0.512	-	0.081	0.513	-

* At 100°F in 30% KOH solution

TABLE IV
CHANGES OF DIMENSIONS AND WEIGHT

Elastomeric Compositions	Before Soaking			After 7 Days Soaking*		
	Thickness Inches	Width Inches	Weight Grams	Thickness Inches	Width Inches	Weight Grams
Shell's S-1509 Specimen No.						
1C	0.083	0.515	6.2517	0.083	0.514	6.2455
2C	0.082	0.518	6.1613	0.082	0.516	6.1530
3C	0.085	0.515	-	0.085	0.516	-
4C	0.082	0.517	-	0.082	0.517	-
Hycar 2001 Specimen No.						
1D	0.078	0.515	6.2982	0.078	0.514	6.2944
2D	0.078	0.515	6.3990	0.079	0.514	6.3954
3D	0.078	0.515	-	0.078	0.512	-
4D	0.084	0.514	-	0.084	0.512	-
Adiprene C Specimen No.						
1E	0.080	0.514	6.2450	0.080	0.515	6.1868
2E	0.080	0.512	6.2435	0.081	0.515	6.1850
3E	0.078	0.513	-	0.079	0.512	-
4E	0.079	0.515	-	0.079	0.511	-
Shell's 305WP Specimen No.						
1F	0.086	0.515	6.3264	0.086	0.515	6.3242
2F	0.084	0.514	6.3083	0.085	0.515	6.3050
3F	0.085	0.515	-	0.086	0.518	-
4F	0.085	0.515	-	0.086	0.517	-

* At 100°F in 30% KOH solution

Four different preparative conditions were studied:

- (1) Degreased bonding surface-elastomer cured at room temperature.
- (2) Degreased bonding surface-elastomer cured at 135-140°F.
- (3) Light sanding of bonding surface-elastomer cured at room temperature.
- (4) Light sanding of bonding surface-elastomer cured at 135-140°F.

The 1/8" overlaps with the 0.002" material were prepared under all four conditions. The 0.003" material was prepared using condition (4) only. Initial room temperature tensile strengths were obtained for each condition. Additional tensile strength tests were conducted after 7 days and 30 days' soaking of the 0.002" specimens in aqueous 30% KOH solutions at 100°F. A 40% KOH solution was used for the 0.003" material.

As shown in Table V, the initial room temperature bond strength was, in all cases, stronger than the silver. After seven days' soak in 100°F 30% KOH solution, the bonds prepared under conditions (1), (2) and (4), above were still stronger than the metal. However, those specimens prepared under condition (3) failed at an average tensile strength of 350 psi -- about one-half the load needed to break the silver foil.

It can be seen that the bond strength is weakened appreciably after 30 days of soaking in 100°F 30% KOH solution for all bonds, except those made by degreasing the Ag and curing the Metlbond 3135 at 137°F for 1 1/2 hours. It is also evident that 40% KOH is somewhat more deleterious to the strength of Metlbond 3135 Ag-Ag bonds than is 30% KOH.

TABLE V

TENSILE SHEAR STRENGTH IN PSI OF Ag FOIL
BONDED TO ITSELF WITH METLBOND 3135

% KOH in Soak	Surface Preparation of Ag and Resin Cure	Initial	After 7-Day Soak	After 30-Day Soak
30	Degreased, R. T.	>670*	>670	287
30	Degreased, 1 1/2 hours at 137°F	>670	>670	>670
30	Light Sanded, R. T.	>670	356	222
30	Light Sanded, 1 1/2 hours at 137°F	>670	>670	350
40	Light Sanded, 1 1/2 hours at 137°F	>837	594	221

* All values in this table designated >670 were metal failures, with the bond withstanding a stress greater than the metal.

b. Bonding of Hycar 1042 to silver foil

Test specimens were prepared by bonding 0.5" x 0.125" x 0.080" pieces of compounded Hycar 1042 to two pieces of 0.5" x 0.002" x 1.5" silver foil at a pressure of 5 psi. The foil overlapped the rubber with one piece on one side and one on the other. Metlbond 3135 was again used as the adhesive. The cure consisted of 24 hours at room temperature and two hours at 135-140°F. These specimens were tested in tensile shear at room temperature. Adhesion failure occurred in each case between the metal and the rubber at an average stress of 300 psi. It is believed that this strength would be adequate in the battery application.

After seven days' soaking in 30% KOH solution at 100°F, an average tensile strength of 179 psi was obtained. The specimens, as before, failed in adhesion. Although this stress level was less than the 300 psi obtained prior to soaking, there is no evidence to show that the Metlbond 3135 was significantly degraded by the KOH solution.

Additional data were obtained after soaking up to 30 days in 100°F 30% KOH solution.

As can be seen in Table VI, extended soaking in KOH solution does appreciably lower the bond strength.

In the actual battery the bonded joints are not stressed in shear; the function of the adhesive is rather to seal against leakage and internal pressure.

Because the bonds still require force to pull them apart after being subjected to a severe environment, it was felt that Metlbond 3135 would prove adequate for bonding the ring seals to the silver electrodes in the NASA battery.

c. Bonding of unrinsed, blotted, KOH soaked Hycar to silver foil

Bonds were prepared in the same manner as above. In this case, however, the Hycar 1042 was soaked in

TABLE VI

TENSILE SHEAR STRENGTH IN PSI
OF Ag-HYCAR 1042-Ag METLBOND 3135
BONDED SPECIMENS SOAKED AT
100°F IN 30% KOH

Preparation of Metal Surface	Initial	After 7-Day Soak	After 30-Day Soak
Degreased	300	179	20.2

40% KOH solution overnight. The pieces of Hycar 1042 were blotted until the surface was dry prior to bonding.

These bonds failed in adhesion at an average stress level of 58 psi compared with 300 psi for the unsoaked rubber.

d. Bonding of HNO₃ etched Ag foil to itself

Ag foil was dipped several times in 1:1 HNO₃ solution, washed with distilled H₂O, dried, and subjected to five minutes at 1000°F.

Tensile shear specimens with 1/8" overlap were prepared using Metlbond 3135 as the adhesive. The bond, as with nonetched Ag, was stronger than the metal. However, the etched Ag was only about one-half as strong as the nonetched Ag foil.

e. Bonding of Hycar 1042 to HNO₃ etched silver foil

Bonds were prepared as previously described, with the silver etched as in paragraph d. Only an average of 147 psi tensile shear strength was obtained prior to KOH soaking -- or about one-half that of the nonetched silver. All bonds failed in adhesion between the rubber and Ag.

It was shown in paragraph b above that Ag-Hycar 1042-Ag Metlbond 3135 bonded specimens lose appreciable strength when soaked up to 30 days in 30% KOH. It was found that similar bonds made with HNO₃ etched Ag, soaked up to 30 days in 40% KOH solution at 100°F, did not lose nearly as much strength as the untreated silver foil (even though their initial strengths were lower). This can be seen in Table VII.

f. Study on the effect on the Ag-Hycar 1042-Ag bond upon cycling in an Ag-KOH-Ag electrolytic cell

An Ag foil electrode 1/2" wide and 2" long was placed into a beaker containing 40% KOH. The

TABLE VII
TENSILE SHEAR STRENGTH (psi)

Ag Surface Preparation	Initial	After 7-Day Soak	After 30-Day Soak
HNO ₃ Etch	147	184	135
Degreased	300	179	20.2

other electrode consisted of the Ag-Hycar 1042-Ag Metlbond 3135 bonded specimens. Both ends of these specimens were used as the electrode to allow any attack on the bond to occur on both sides of the bond at the same time. The cell was operated at 25-50 milliamps. For each cycle electrolysis was allowed to proceed until gas bubbles were in evidence. A control specimen was present in the bottom of the beaker while cycling took place. The results obtained are shown in Table VIII.

It can be seen that the strength of the bond between the silver and rubber is affected by the cycling process.

The metal surface underneath the bond showed considerable deposition of Ag_2O and Ag_2O_2 . The amount of this deposition generally increased as the number of cycles increased.

g. Study of the effect on the etched Ag-Hycar 1042-etched Ag bond upon cycling in an Ag-KOH-Ag electrolytic cell

The same experiment as in f was carried out, but with etched Ag foil used in place of nonetched Ag. This was done because greater resistance to KOH attack had been shown by Ag foil-Hycar 1042-Ag foil bonds made with etched Ag (see Table VII). The results of this cycling study are shown in Table IX.

It is evident that there is essentially no loss in tensile shear strength due to electrolytic cycling of etched Ag-Hycar 1042-etched Ag bonds.

3. Cell Assembly

Two methods of cell assembly were investigated. As described below, neither method produced acceptable results.

TABLE VIII

TENSILE SHEAR STRENGTH
VERSUS ELECTROLYTIC CYCLING

No. of Specimens	No. of Cycles	Tensile Shear Strength (psi)
1	0	94
1	4	9.4
1	8	74
1	12	30
1	20	Broke while placing in test fixture

TABLE IX

TENSILE SHEAR STRENGTH
VERSUS ELECTROLYTIC CYCLING

<u>No. of Cycles</u>	<u>Tensile Shear Strength (psi)</u>
0	212
4	178
8	197
8	186
12	58
12	226
20	132
20	184
28	198

a. Preparation of battery-like cells and inserting the electrolyte with a hypodermic needle

Two types of cells were constructed. The first consisted of an Ag foil, rubber ring seal, Ag foil sandwich. Hycar 1042 was used to make the 0.015" thick ring seal. Metlbond 3135 was used as the adhesive.

With a 0.012" diameter hypodermic needle (Figure 5) it was possible to inject 40% KOH into three out of six of the cells prepared without cell damage. No leakage was observed with the three good specimens, as determined by placing the injected cells in distilled H₂O and noting pH changes.

The second cell configuration more closely approximated that envisioned for the actual battery. It consisted of five layers. The first layer was a circular piece of 0.002" Ag foil. The next, a 0.015" thick Hycar 1042 ring seal; the next was a stack of circular (6) layers of cellophane surrounded by a small 0.015" thick Hycar 1042 ring seal; the next, another 0.015" thick Hycar 1042 ring seal; and finally, another round piece of 0.002" Ag foil. All of these layers were bonded with Metlbond 3135. (See Figure 6).

As above, it was possible to inject 40% KOH into these cells using a 0.012" diameter hypodermic needle. About 50% of those made leaked or were ruined in the injection process.

b. Wet assembly of a battery-like cell

Several circular-shaped cells, like those fabricated previously for testing out the injection method of adding the electrolyte, were prepared. First, the 0.015" thick Hycar 1042 seal was bonded to the 0.003" thick Ag foil. This was filled with 40% KOH and a layer of nylon cloth. In spite of the fabric the KOH ran over the rubber seal making it difficult to bond the next layer. This consisted of six pieces

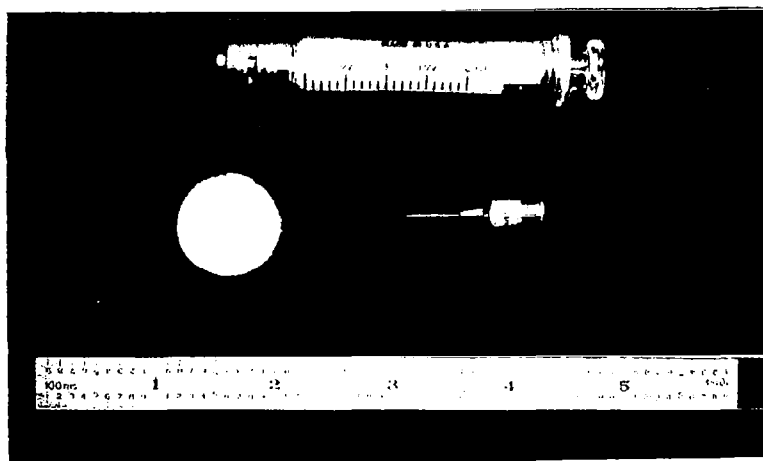


Figure 5. Hypodermic Needle

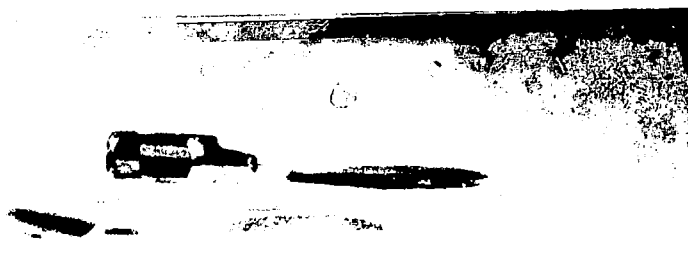


Figure 6. Cell Sample and Needle

of cellophane surrounded by 0.015" thick Hycar 1042 ring seal. This half cell was then cured in the oven. The upper ring seal and Ag disc were then bonded after filling the remainder of the cell with KOH and a piece of nylon cloth to soak up as much of the KOH as possible.

Most of the cells were so poorly bonded because of the presence of the KOH on the surfaces that they readily leaked when placed in distilled H₂O. This occurred in spite of the fact that all surfaces to be bonded were blotted prior to bonding.

B. Cell Container Development

Due to problems associated with the duplex plates, gas elimination and ion exchange membrane, the original concept of the cell design could not be realized within the scope of this contract. It was decided, therefore, to change the battery cells to a more conventional design.

1. Container Design

The new design utilizes a cell container in which the electrodes and electrolyte are sealed. Figures 7 and 8 show the cell containers and the covers for them.

Some difficulties were encountered in cementing the lids on the containers, and sealing the leads where they come through between the containers and lids. Therefore, the cell container was modified to that shown in Figure 9. The electrical leads are brought out of the cell and sealed, and the lid is bonded to the container before the electrolyte is put into the cell container. The electrolyte is added through the small hole in the center of the flat side of the cell. This hole is sealed by bonding in a small plug. This small plug is considerably easier to bond and seal than the lid.

2. Container Material Studies

Narmco conducted a literature survey of water permeability of various plastics. Most of the available information is for

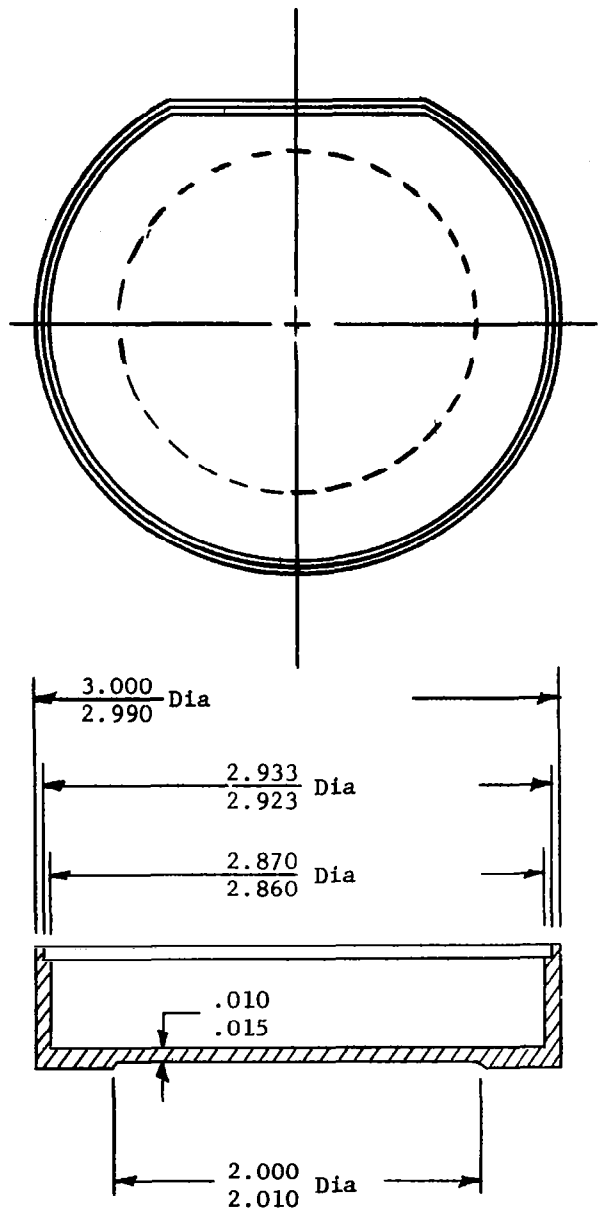
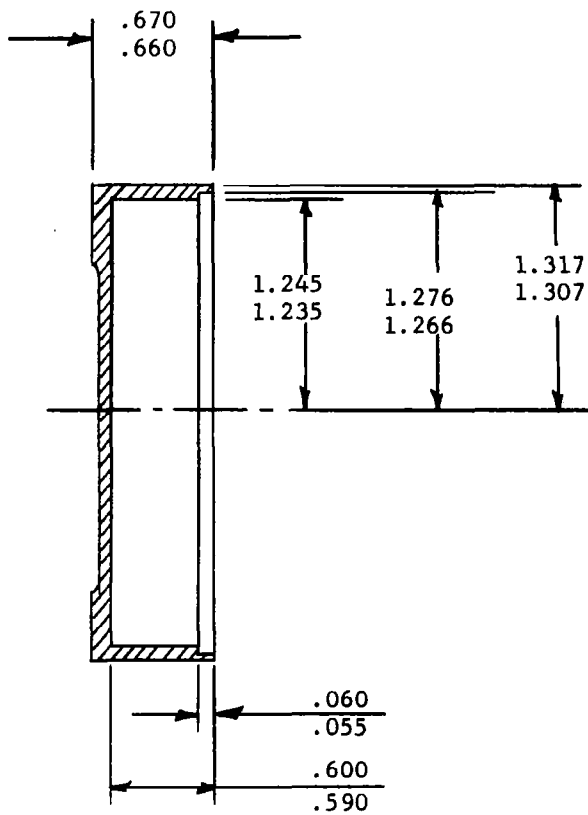


Figure 7. Cell Container

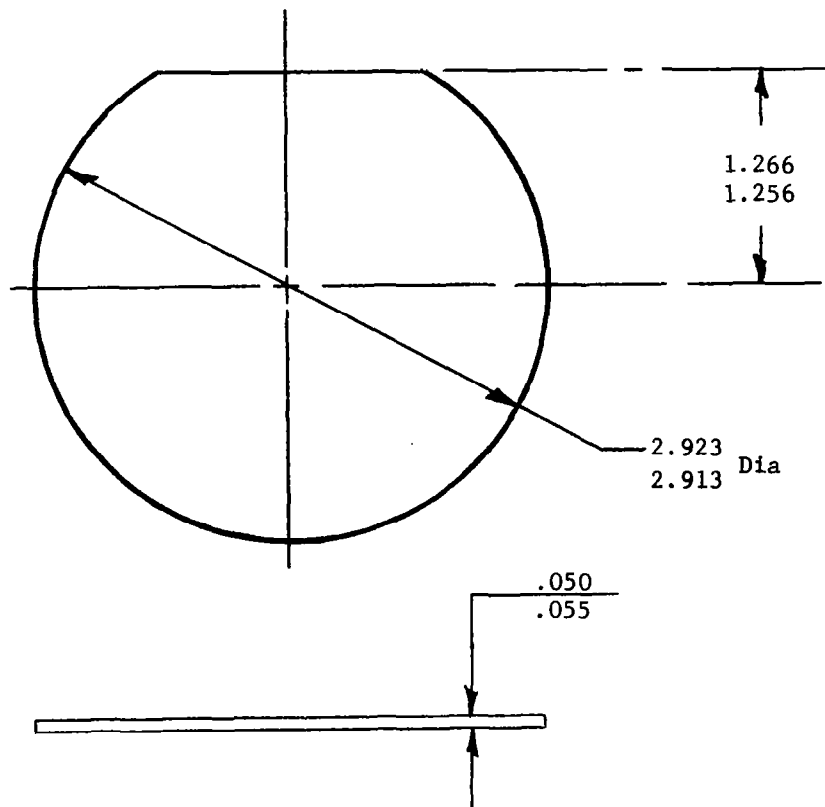


Figure 8. Cover, Cell Container

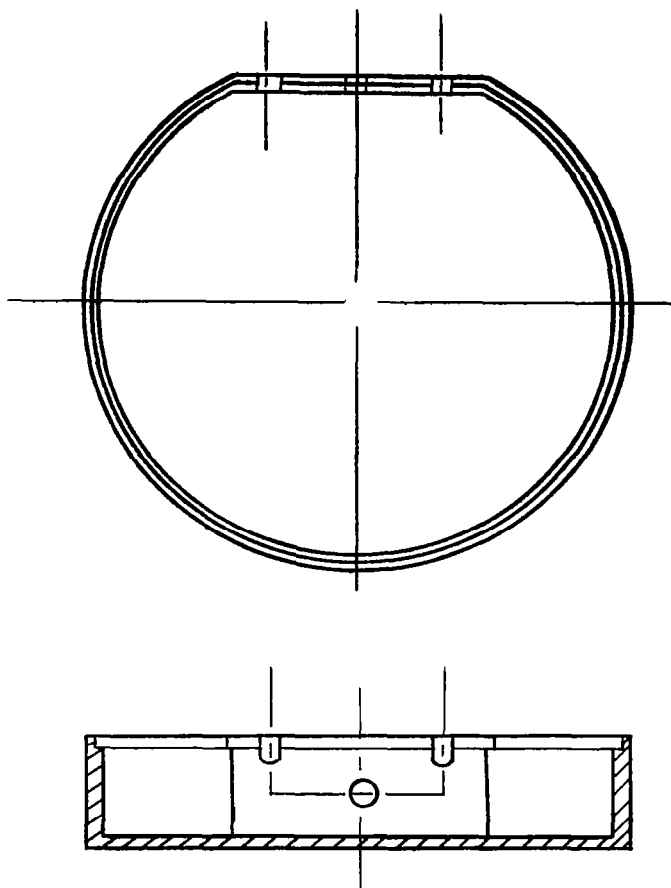


Figure 9. Revised Cell Container

film materials as used in packaging, etc. Unfortunately, all of the potential molding resins have not been evaluated, or at least their permeability data are not reported. Nevertheless, the materials for which data does exist suggest definite trends from which a workable material for the NASA cell could be selected. The summary of this study is shown in Table X. It is obvious that the better plastic materials from a water permeability standpoint are those which are hydrophobic, such as polyethylene, Teflon, Kel-F, etc. In addition, there are subtleties which these attached data do not point out, such as density and molecular weight effects. One would expect polyethylene to be better than it is on a hydrophobic basis, but due to its low density, it is more permeable than most other hydrocarbon or halocarbon polymers. Polystyrene is particularly bad in this regard.

The hydrophilic polymers such as Mylar, nylon and polymethylmethacrylate are generally more permeable than the hydrocarbons, however, the high molecular weight of nylon and Mylar plus the associated hydrogen bond linkages appear to make these polymers intermediate to the best and poorest hydrocarbon polymers.

Since all of the polymers tabulated, except Mylar (a polyester) are reported to be resistant to KOH, it was felt that the selection of a resin for manufacture of the cell cases could be made on the basis of low water permeability, moldability, bondability, and cost. It further appeared to be desirable to add epoxy resins to the list of those to be considered. Although no permeability data was found for this class of resins, based upon their chemical and physical properties, one would expect these to be about the same as nylon.

All of these resins can be molded except Teflon TFE. Only epoxy, polystyrene, and polymethylmethacrylate can be cast. Since the chance of bubble occlusion or voids is high in a casting process, the resultant production difficulties would probably outweigh any mold cost savings. So, with the acceptance of molding as the forming process, the only considerations other than permeability are bondability and cost. On this basis, both the halocarbons and nylon are at a definite disadvantage. This leaves Saran

TABLE X

PERMEABILITY DATA SUMMARY

Rating	H ₂ O gms/mil/100in ² /day/atm	N ₂ cc/mil/100in ² /day/atm	O ₂ cc/mil/100in ² /day/atm
1	Polychlorotrifluoroethylene 1.3	Polyvinylidene chloride .86	Polyvinylidene chloride 3.0
2	Polyvinylidene chloride 3.0	Polyethyleneterephthalate 1.2	Nylon 6 5.5
3	Polyfluoroethylene propylene 3.9	Nylon 6 1.7	Polyethyleneterephthalate 5.6
4	Polytetrafluoroethylene 4.4	Polychlorotrifluoroethylene 9.5	Polychlorotrifluoroethylene 30
5	Polyethylene 14	Polystyrene 45	Polyvinylchloride 123
6	Polyethyleneterephthalate 25	Polyfluoroethylene propylene 52	Polyethylene 416
7	Nylon 6 181	Polyethylene 101	Polyfluoroethylene propylene 465
8	Polyvinylchloride 186		Polystyrene 1007
9	Polystyrene 351		
10	Polymethylmethacrylate 738		

(polyvinylidene chloride), polystyrene and epoxy. Although epoxy molding systems would have better thermal properties and bondability than Saran or polystyrene, Saran would be serviceable to 160°F, and it can be bonded with epoxy polyamide resins or solvent welded. Furthermore, it has excellent water permeability characteristics and perhaps, just as important, it has the lowest gas permeability of any known plastic. This characteristic might well be important in the operation of the sealed battery in space.

For the purpose of receiving more accurate information on the resistance of Saran to 40% KOH, tests were conducted in the presence of oxidizing agents (H_2O_2). During these tests a darkening effect was observed and, in spite of the good permeability and process characteristics, other materials than Saran must be considered.

A further evaluation of various potential cell case materials was conducted using Power Sources supplied styrene cases as received and coated with about 10 mils of Saran F-120, as well as cases fabricated from .075" sheet stock molded from Narmco Resin 3135 epoxy-polyamide and Saran F-120. These cells were all rectangular. The styrene cases were 4 1/8" high x 2 1/4" wide x 3/4" thick. The Saran and 3135 cases were 4 3/4" x 2 3/8" x 7/8". The cell cases were filled half full with 40% KOH and sealed by bonding the lids on with Resin 3135. The cells were placed into a 120°F oven and weighed daily. Each system was run in triplicate. The results were compiled on the basis of grams (loss) per 100 square inches per day per atmosphere. The averages for each system are plotted in Figure 10. With the exception of the high weight loss for the Saran coated polystyrene cases, which may be due to absorbed methyl ethyl ketone solvent attack of the styrene during coating, the results are pretty much as expected.

Additional studies were conducted to evaluate the chemical resistance of the case materials to the cell components. Saran must be ruled out on this basis since it is slowly darkened in contact with the electrolyte and it precipitates free silver from an alkaline solution of the silver oxide.

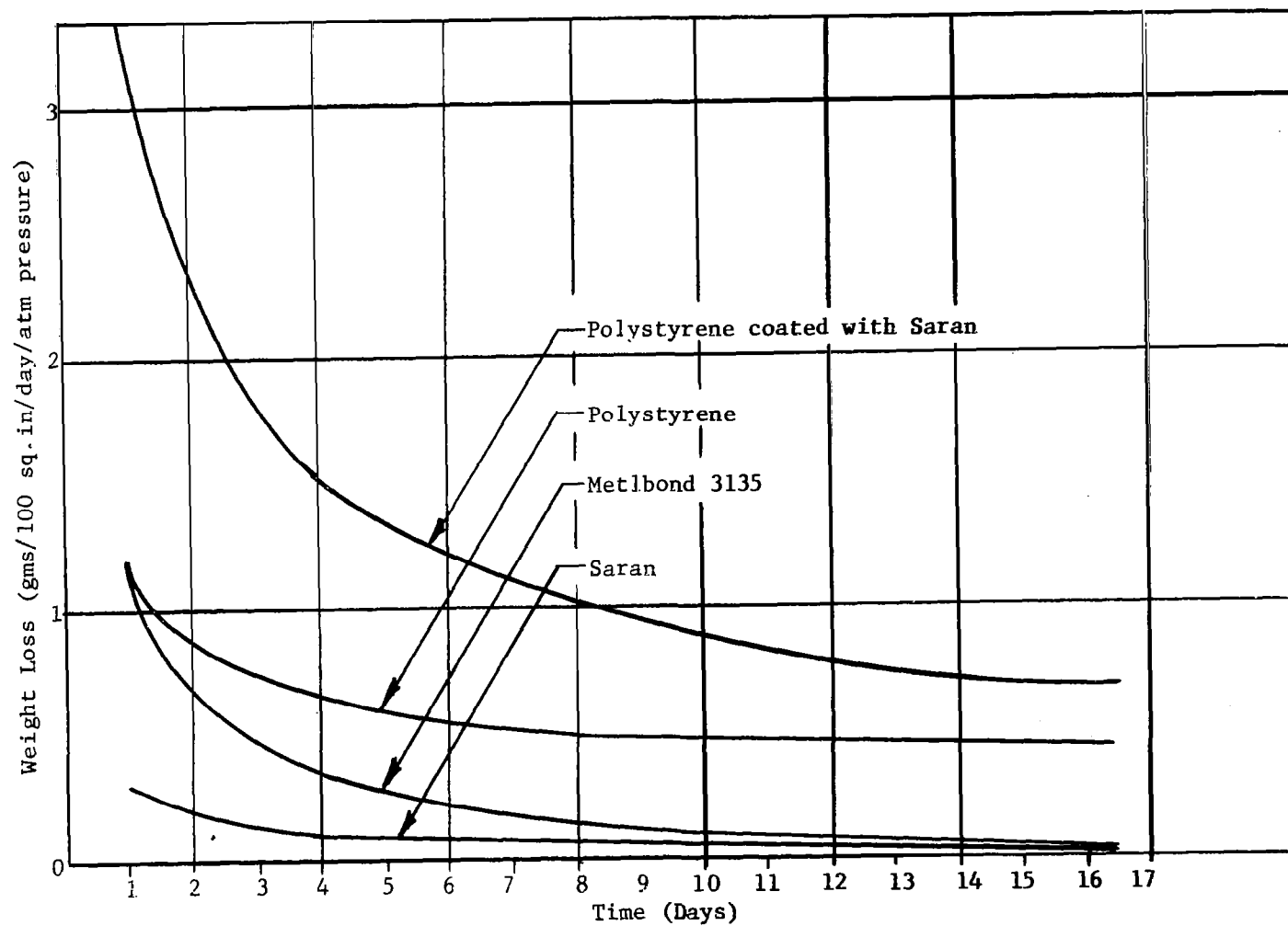


Figure 10. Permeability of Plastics for 40% KOH at 120°F

Resin 3135 is almost as good in permeability as Saran and it is chemically resistant to the cell materials. A material tentatively chosen for fabrication of the cell containers was an epoxy-polyamide resin system consisting of 60 parts Epon 820, 40 parts Lancast "A" and 2 parts DTA. This material is very similar to Resin 3135. Several cells were fabricated with this material and sent to Power Sources Division for evaluation.

Power Sources evaluated the chemical resistance of the supplied cell cases. They found that a silver deposit resulted after a 24-hour immersion in silver oxide saturated 30% KOH at 120°F. Narmco's previous studies conducted at room temperature failed to show this reaction with Resin 3135 system, first considered. Subsequent tests were performed at Narmco on Resin 3135 and the Epon 820-Lancast A - DTA (60-40-2) at 120°F and verified the reaction of both these systems with the silver oxide solution. Therefore, in spite of the improved permeability afforded by the epoxy-polyamide system, styrene was the final choice for the cell case material.

C. Case Development

This part of the program was initiated to engineer the filament wound battery case which would meet the requirements regarding internal pressure, impermeability, weight, and assembly process of the battery.

1. Structural Integrity

During the selection of the case material, the question came up in respect to the stability of the plastic material in outer space environment. A literature survey was made. Significant work in this area has been conducted by Norman E. Wahl of Cornell Aeronautical Laboratory. This report on "The Effects of High Vacuum and Ultraviolet Radiation on Plastic Materials," Contract AF 33 (616)-6267, WADD T. R. 60-125, indicates that epoxy laminates would be satisfactory for space environments. Effect of vacuum in the order of 10^{-6} to 10^{-7} mm Hg and ultraviolet flux ranging from $1/3$ to $2\ 1/2$ times the solar constant of two calories per cm^2 per min. were investigated. The equilibrium temperatures depended upon the

intensity of the ultraviolet radiation and ranged between 250 to 465^oF. It was found that the effect of U. V. radiation is more severe than the effect of vacuum. The decrease in strength of the resin was not significant. It was concluded, therefore, that a battery case which has a high strength safety factor and is probably within a vehicle which protects it from radiation, will not experience a significant degradation due to the space environment.

The preliminary inside diameter of the battery case was selected as three inches. Two approaches have been used to establish the winding method and the integrity of the case.

First, a steel mandrel was designed and manufactured which permitted the winding of cases with one open and one closed end which served to establish the preliminary winding pattern and case strength. An end plate and a test plug were designed and machined. The first and second cases were wound on this mandrel. The first case was wound with helical winding only. In spite of a slightly tapered mandrel, the case was very difficult to remove from the mandrel.

The plug was bonded into the open end and the case pressurized with water. At 120 psig, the case started to leak around the end plate joint and the test was interrupted. The winding pattern and integrity of the case appeared satisfactory.

The winding of the second case served for study of silver lead sealing. The second case had a different winding pattern. There was one layer of circumferential windings in order to permit penetration by the silver ribbon. The ribbon was then bent on top of this layer and the winding was completed with a helical pattern. After curing, the case was sectioned and the area around the lead inspected. Microscopic investigations and peeling of layers revealed that the bond between silver and resin was inadequate. The reason for this was the contamination of the silver surface. It will be attempted to improve the bond by a different cleaning method of the silver; i. e., it is planned to wipe the grease off with MEK, clean for a few seconds with Nitric Acid, rinse and dry for five minutes at 1000^oF.

The third case was wound on a different type of mandrel. This mandrel was slush molded from DMM (Disintegrating Mold Material) in a tubing and dried. Two end plates were wound in, using circumferential and improved helical winding patterns. One end plate had a steel pressure fitting. After curing, the mandrel was washed out. The case was pressurized with water and developed some leakage. The test was interrupted at 120 psi pressure.

These tests showed that the attachment of the end plates is a critical area and requires some reinforcement. The weight of Case Number 3 (two end plates and the shell) was 0.25 pounds. The initial cases are presented in Figure 11, and are, from left to right: Pattern study, first case, third case. Figure 12 shows the third case and the pressure fitting.

Case Number 4 was wound with reinforcing circular winding at the ends. During pressurization no leakage developed in this area, but some minute leaks in the center of the case occurred. In order to use this case for structural tests, a thin coat of an elastomer resin was slush-molded to the inside. The case was pressurized with water and the end plate failed at 130 psi pressure (see Figure 13).

The failure of the glass flake composite pointed to overstressing of the tension side, and it was decided to mold the end plates with a fibrous reinforcement on one face. For this purpose one layer of Scotchply isotropic cloth was used which has proven to be very effective for bending applications of glass flake composites. This construction was utilized in the construction of all future end plates.

In an effort to produce a denser structure to reduce the leakage through the case wall, different glass roving was tried. The new roving consisted of 51 filaments per end compared to 204 for standard single end roving. The filament diameter in the new roving was 0.00021" compared to the standard of 0.00036".

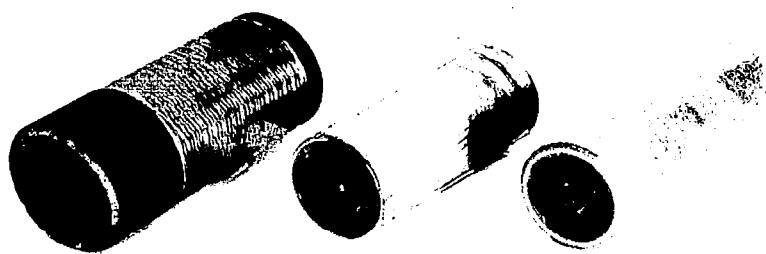


Figure 11. Battery Case Development

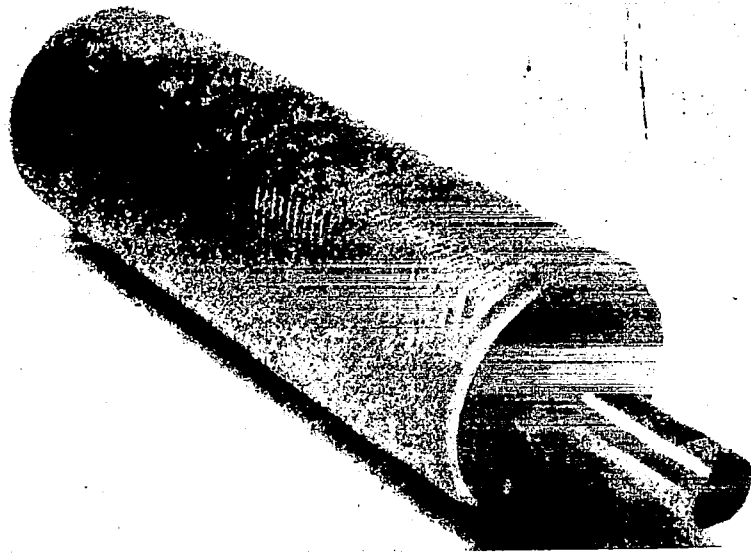


Figure 12. Experimental Battery Case



Figure 13. End Plate Failure of Case Number 4

Case number 5 was wound with this thin fiber. Some difficulty was encountered in using this fiber as it broke several times during the winding operation. Also, it was very difficult to handle and to distinguish from the surrounding resin after it was laid on the mandrel. In spite of the fact that this thin fiber was used which produced a denser structure, leakage occurred during pressure testing.

The inside of the case was again coated with an elastomeric resin and the tests repeated. The case failed in axial direction at 125 psi. The mode of failure is shown in Figure 14 and is very unusual for a pressure vessel. It was felt that the failure was due to an inferior quality of the fine fiber. Due to this failure and the difficulty in processing the thin fiber, it was decided to use the standard single-end HTS roving for future cases and to prevent leakage by other methods.

Case number 6 was wound with standard fiber. This case was purposely wound overweight in order to test the strength of the new end plates. A coating of elastomeric resin was applied from inside by slushing. In spite of minute leakage during pressure testing, the internal pressure could be held for five minutes at 150 psi then gradually increased up to 500 psi. At this pressure the end plate on the fitting side, for which the original nonreinforced flake laminate was used, failed in shear.

This case was cut longitudinally and inspected. Visual examination revealed that the resin of the case had minute strain cracks; however, the inner coat of the elastomeric resin maintained its integrity. This observation indicated a possible solution for the leakage problem of the experimental cases. It was reasoned that microscopic cracks were already developing under lower pressure, causing premature leakage. It was believed that a modification of the winding resin system, making it more elastic, would help prevent the development of these cracks. It was decided to use such a resin for the next case.

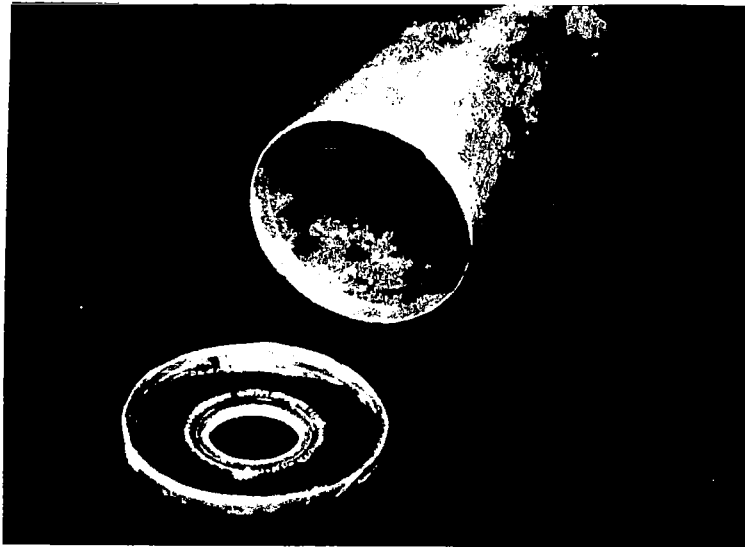


Figure 14. Cylinder Failure of Case Number 5

Case number 7 was wound with standard fiber and a more elastic resin, consisting of 50% Epon 820 and 50% Lancast A. The helix angle was 52° and the density of reinforcements 30 ends per inch. After cure, the case was tested with Freon gas leak detector as well as with water with the following results:

- a. Minute leakage was detectable at 3 psi Freon pressure and the areas were noted.
- b. The same spots noted in item (a), plus some additional areas, leaked at 20 psi water pressure, but pressure could be increased to 150 psi in spite of leakage.
- c. A gel-coat of identical resin was slush cast inside the case, cured, and the case was tested again.
- d. Leakage began to develop at 150 psi.
- e. Helical fibers failed at 275 psi.
- f. No detectable cracks have developed in this resin in spite of high pressure.

This test proved that the elastic resin was superior to the previously used rigid system, but that the thin composite shell was not capable of holding the required pressure without leakage. It was, therefore, decided to introduce a film as a leak barrier.

Case number 8 was wound with Du Pont Teflon FEP film and with two silver leads between the fiberglass layers. After curing and removing the mandrel, it was tested with Freon as well as with water with the following results:

- a. No leakage was detectable at a Freon pressure of 20 psi.
- b. At 150 psi water pressure some spots at the end plate joints began to leak. No leakage in the cylindrical portion of the case or around the leads occurred.

- c. Subsequent test with Freon at 65 psi indicated that the rate of leakage in these spots varied from 0.4 to 5.0 ounces per year.
- d. The total weight of the case (shell and end plates) was 0.27 pounds.

This test proved that the Teflon film is a more effective leakage barrier than the gel-coat. It proved also that an improvement of the structure at the end plate joint was necessary. It was believed that the main reason for leakage in this area is the nonuniform fiber distribution due to slippage during the winding operation.

Case number 9 was wound with redesigned end plates utilizing a larger radius. This new configuration proved to be effective in reducing fiber slippage. This case was subjected to the following tests:

- a. Hydrostatic test at 150 psi. No leakage was detectable after five minutes at this pressure.
- b. Freon gas test at 50 psi. No leakage detectable.
- c. Freon gas test up to 150 psi. Up to 140 psi no leakage was detectable. During pressure increase to 150 psi leakage occurred at a rate of approximately five ounces per year. The leak was at one spot at the end plate joint opposite the fill fitting.
- d. Hydrostatic test to burst. At 150 psi slow formation of water drops appeared at the spot of leakage detected under item (c), but pressure could be increased up to 310 psi without more leakage. At this pressure the fitting end of the case failed in longitudinal tension.

At this point in the program it was felt that the structural integrity of the case was satisfactory. The burst pressure of the cases was well above the minimum required.

2. Impermeability

During the fabrication and testing of the nine cases described above, the permeability of the case walls was gradually reduced. The first cases leaked at very low pressure levels. The addition of a gel-coat in the case improved this leakage slightly. A change in end plate design, to reduce fiber slippage in this area, the substitution of a plastic film, FEP Teflon, in place of the gel-coat, and a change to a more flexible winding resin reduced the case permeability almost to an acceptable level.

It must be pointed out that all cases fabricated up to this point were made on a removable mandrel. After removal of the mandrel, the cases, which had a wall thickness of 0.010" to 0.020", were somewhat flimsy. With the change in cell design, and the inclusion of a cell container in the battery construction, the actual cases would have considerably more stiffness than the test cases. Therefore, it was decided to proceed with the fabrication and test of several dummy batteries.

D. Dummy Batteries

Several dummy batteries were fabricated for vibration and KOH permeability testing. The first of these was fabricated prior to the final choice of styrene for the cell container material. The containers for this battery were of epoxy polyamide. The individual cell containers were filled with sheets of 1/16" thick neoprene rubber and one 1/16" thick sheet of lead. Eleven cells were assembled to a dummy battery. The average weight of each loaded cell container was 145.1 grams with an average dummy weight of 124.1 grams. This corresponds to an average weight of 21 grams for the empty container and lid. The end plates were made 1/4" thick to accommodate the O-ring seal. The integrity of 1/8" thick end plates had been established by previous tests. The lids were bonded to the container with Narmco Resin 3135. The same resin was used for joining the containers and the end plates. The assembled battery was mounted on the lathe for winding. Next, Du Pont Teflon FEP film and glass roving were wound over the cell container assembly. After curing, the weight of the battery without

shaft (used for pressure and permeability tests) was measured as 3.90 pounds. Figure 15 shows the finished dummy battery. Note the transparent shell which makes the cell containers visible in the illustration.

In order to determine whether there was any gross leakage, the battery was immersed in water and internal air pressure of 75 psi was applied during a period of five minutes. No leakage was detectable. The battery case was then filled with a 40% by weight aqueous potassium hydroxide solution and held at a constant pressure of 75 psi, with nitrogen, for a period of eight days at a temperature of $120 \pm 5^{\circ}\text{F}$. The test was performed using the apparatus illustrated in Figure 16.

A low pressure nitrogen stream enters the system at drying flask A, where any moisture in the gas is removed by adsorption with indicating Drierite. A "T" in the nitrogen line allows the gas to flow through control cylinder C and permeability test cylinder D. The control cylinder provides a means to correct for the presence of moisture in the system, which is not due to battery case permeability.

The battery case E is fitted with a steel pipe with openings inside the case. With the use of a vacuum line a 40% KOH solution was drawn into the case until it was completely full. One end of the pipe was plugged and the battery case was sealed in the test cylinder. A nitrogen line was attached to the open end of the pipe and the interior of the case held at 75 psi throughout the test period.

The oven B was heated to $120 \pm 5^{\circ}\text{F}$ and a thermocouple F was soldered to the permeability test cylinder to provide accurate temperature monitoring.

Any moisture present in cylinders C and D is swept from them, by the dry nitrogen stream, into drying flasks I and J, where the water is adsorbed by indicating Drierite. These flasks are vented to flask K which is filled with glycerine to prevent any moisture from going back into the system. In addition, it provides a convenient flow rate indicator, since the nitrogen bubbling through the glycerine is readily apparent.

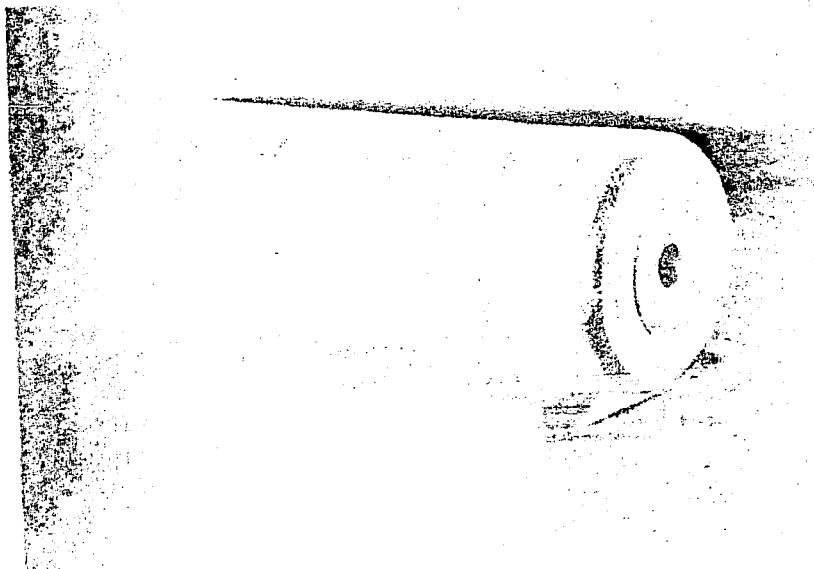


Figure 15. Dummy Battery Number 1

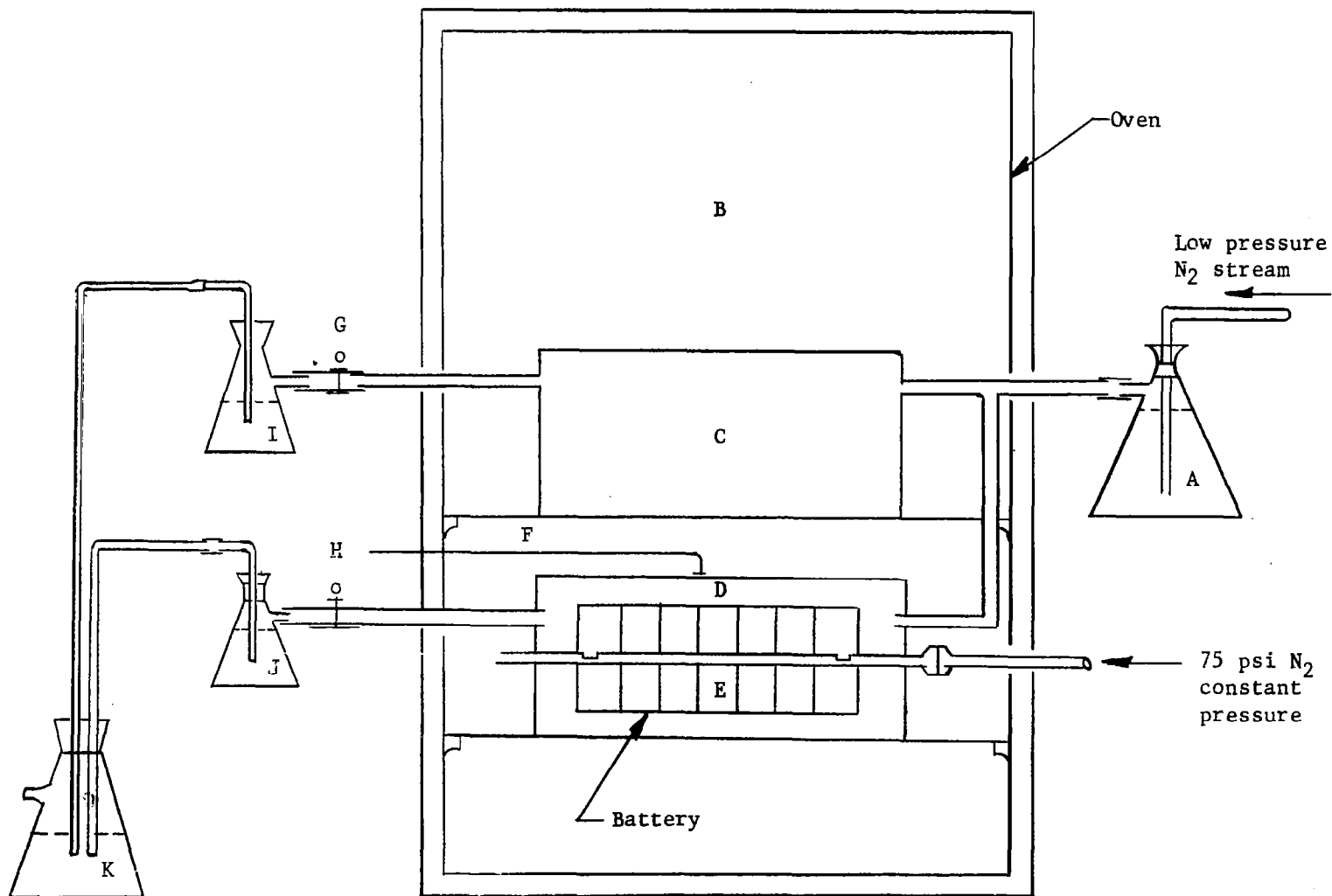


Figure 16. Permeability Test Apparatus

Drying flasks I and J were removed from the system and weighed at 24 hour intervals for a period of eight days. The low pressure nitrogen stream was turned off and screw clamps G and H were tightened over the rubber tubing to seal the system. The drying flasks were disconnected and immediately sealed with preweighed caps, so that exposure of Drierite to atmospheric moisture would be negligible.

The moisture pick-up was determined by weighing both flasks on an analytical balance to an accuracy of 0.0001 gram. The moisture pick-up of the control flask I was subtracted from test flask J to correct for the presence of moisture due to causes other than permeability of the battery. Table XI gives the moisture pick-up as measured by determining the increase in weight of drying flasks I and J. Figure 17 shows this increase in weight in the test flask as a weight loss for the battery in a graphical form. After these tests the dummy battery was shipped to Power Sources for vibration testing. This case, however, was damaged in shipment and could not be vibrated.

The second dummy battery was wound using new styrene cell containers, but otherwise with identical processes established by previous winding operations. After the case was cured at 150°F it was evident that a separation had occurred somewhere in the composite case layup. Upon dissection it was determined that this separation had taken place at the Teflon film styrene cell interface. The adhesive (the filament winding resin system is Epon 820 - Lancast A 50-50) remained with the Teflon film-fiber composite and did not bond to the styrene surface.

The investigation also established a definite distortion in the styrene cells in the unsupported areas between cell ends. The cause for failure was tentatively placed upon poor adhesive peel strength and on the distortion resulting from the 150°F cure, since the heat distortion temperature of the styrene is a nominal 160°F. A bonding study was therefore initiated: 5-mil treated Teflon FEP film was bonded to flat styrene sheets to test the peel strength of a variety of adhesive systems and styrene surface treatments. The initial studies included:

- Epon 820 - Lancast A, 50-50 Control
- Epon 820 - Lancast A, 80-20 (Epoxy-polyamide)
- Resin 3135 - Curing Agent 7111, 50-50 (Epoxy-polyamide)

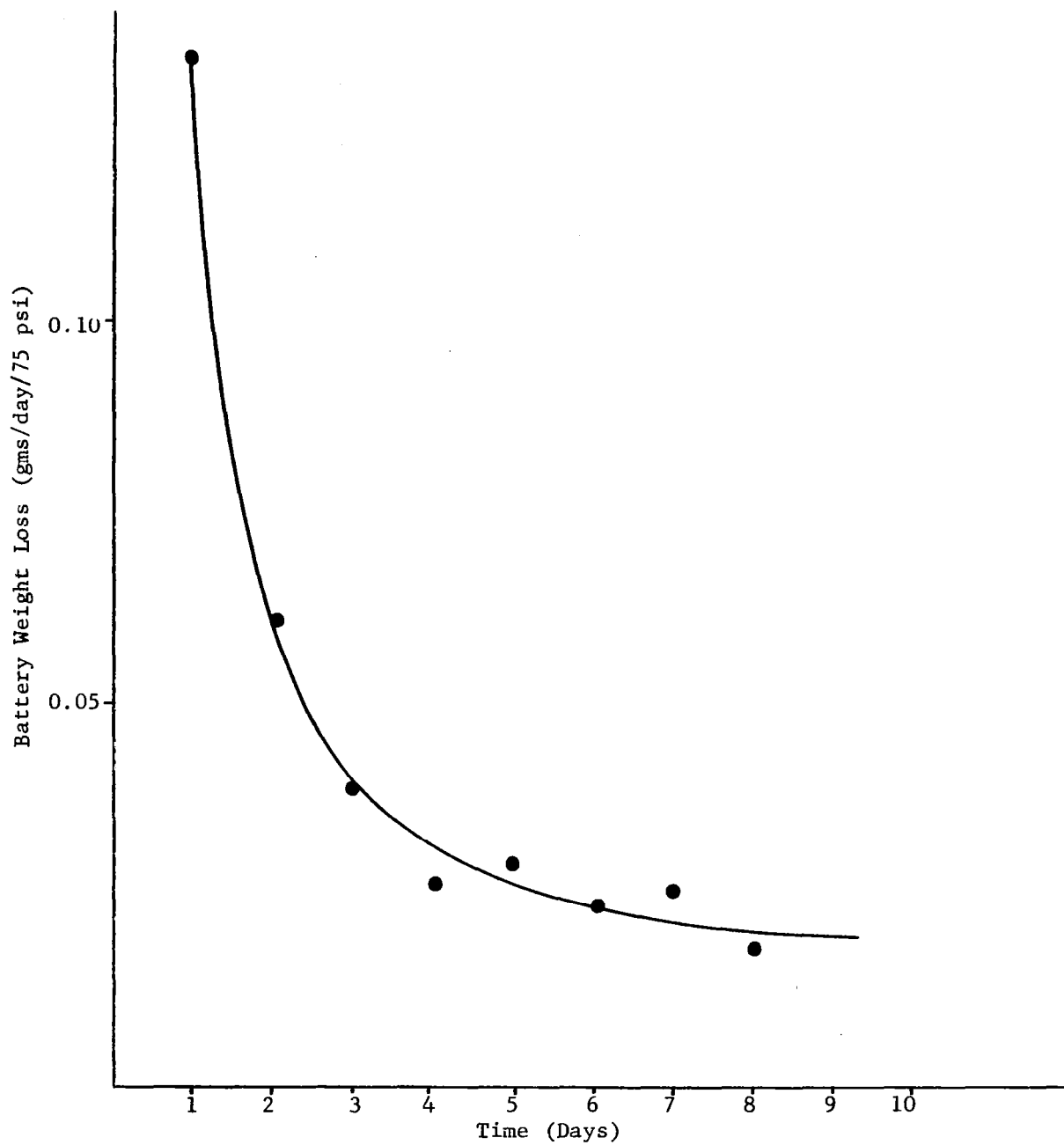


Figure 17. KOH Permeability Test

TABLE XI

KOH PERMEABILITY OF
DUMMY BATTERY NUMBER 1

Elapsed Time Days	Test Drying Flask J - Increase in Weight, grams	Control Drying Flask I - Increase in Weight, grams	Total Net Increase in Weight, grams J - I	Increase in Weight per 24 hours
1	.2074	.0738	.1336	.1336
2	.2874	.0933	.1941	.0605
3	.3309	.0984	.2325	.0384
4	.3638	.1046	.2592	.0267
5	.3970	.1088	.2882	.0290
6	.4226	.1110	.3116	.0234
7	.4517	.1151	.3366	.0250
8	.4702	.1161	.3541	.0175

Styrene Cement
Polylite 8037 (Polyester)
X-305 (Epoxy adhesive)
Resin 3135 - Curing Agent 7111, 50-50 plus 5% Styrene
Monomer
Resin 7343 - Curing Agent 7139, 100-11 (Polyurethane
adhesive)
Styrene Monomer Etch with Resin 3135
Sodium Dichromate Sulfuric Acid Etch with Resin 3135

These systems were all cured at room temperature. The styrene cement and polyester both adhered well to the styrene but failed readily in peel to the Teflon film. All other systems failed readily to the styrene except the 80-20 Epon 820 - Lancast A system and Resin 7343 polyurethane. Subsequent four-hour at 125°F cures, involving various combinations of these latter two systems, verified the superiority of the polyurethane system even as a primer for the 80-20 Epon 820 - Lancast A system.

Since the case fabrication step was best accomplished as a single layup and cure operation to avoid excessive thickness associated with a separate film application and cure, the use of the polyurethane system alone was undesirable. If it were to be used, it would, no doubt, migrate into the filament-resin system during winding. This was undesirable due to its extreme reactivity with amines such as Lancast A. Consequently, it was decided to employ a polyurethane adhesive prime as a separate 125°F cured coating over the styrene containers. It would be followed by the Teflon film with the 80-20 Epon 820 - Lancast A system and the subsequent filament winding with the previously used 50-50 Epon 820 - Lancast A system.

The entire wound shell was removed from the second dummy battery, and the cells ground to a uniform diameter. The case was then rewound utilizing the following process:

1. Cleaning with isopropanol and priming the assembly with a 2-mil thick coating of Adiprene L100 (L100-11, MOCA-1).
2. Gelling for two hours under constant rotation.
3. Advanced gelling for three hours under constant rotation and heat, not to exceed 125°F, supplied by heat lamps.

4. Final oven cure at 125°F for 14 hours.
5. Wrapping of 0.002" thick and 1.00" wide Teflon FEP tape using a resin system of 80% Epon 820 and 20% Lancast A. The ends of the tape were secured by drops of Eastman Kodak 910 adhesive. Tape was wound over a brush coat of the above resin and a tape overlap of 0.25" was maintained.
6. Filament winding with single-end 150/HTS glass roving using a resin system of 50% Epon 820 and 50% Lancast A.
 - One layer of circular wrappings 0.75" wide at both ends of the case at a tension of 0.50 pound per end. Longitudinal speed -- 0.0083 in. / revolution.
 - Three layers helical wrappings at 40° angle to the battery axis. Mandrel rotation -- 56 RPM, traverse countings -- 28 per minute, total traverse cycles per three layers -- 741 counts.
 - One layer of circular wrappings full length.
 - One layer of circular wrappings 1.00" wide at both ends.
7. Repeat gelling operation as described in items 2 and 3.
8. Curing in oven at 125°F for 14 hours.

The weight of liner and filament wound shell was 51 grams.

The rewound dummy battery number 2 was subjected to the following tests:

1. The battery was immersed in water and pressurized with 75 psi air pressure for five minutes. No leakage was detectable.
2. Low temperature test: The battery was soaked for three hours at -20°C. After removing from the freezer it was checked for possible voids by tapping it from outside. This released apparent internal stresses and the cast bar separated from the structure at one end of the battery. It appeared that the coefficients of thermal expansion were not compatible and it was decided to make the flat section bar from polystyrene.

3. KOH-Permeability Test: This test was performed as before with dummy battery number 1, except that it was interrupted after three days. The permeability change is shown in Table XII.

TABLE XII
KOH PERMEABILITY OF
DUMMY BATTERY NUMBER 2

Elapsed Time Days	Weight Increase in Flask per 24 hours
	(grams)
1	0.0921
2	0.0749
3	0.0544

Figure 18 shows the diagram of the battery weight loss with time. It is obvious that the styrene container has a somewhat higher permeability than the previous epoxy container. In extrapolating the curve it might be assumed that an equilibrium will be reached after eight days, after which time the rate of leakage will be 0.033 grams per day approximately. With a battery diameter of 3" (0.076 m) and a length of 8" (0.203 m) the total battery case area is 0.057 m^2 . Therefore, the daily loss per square meter is $0.033/0.057 = 0.58 \text{ grams}$, or only about 40% of the still acceptable level of $1.5 \text{ grams/day/m}^2$ as specified in the original requirements.

After the above tests the dummy battery was sent to Power Sources Division for vibration testing.

The dummy battery number 2 (case number 10) was returned to Narmco after it was vibration tested and helium leak tested at Power Sources. The leakage rate, measured by helium

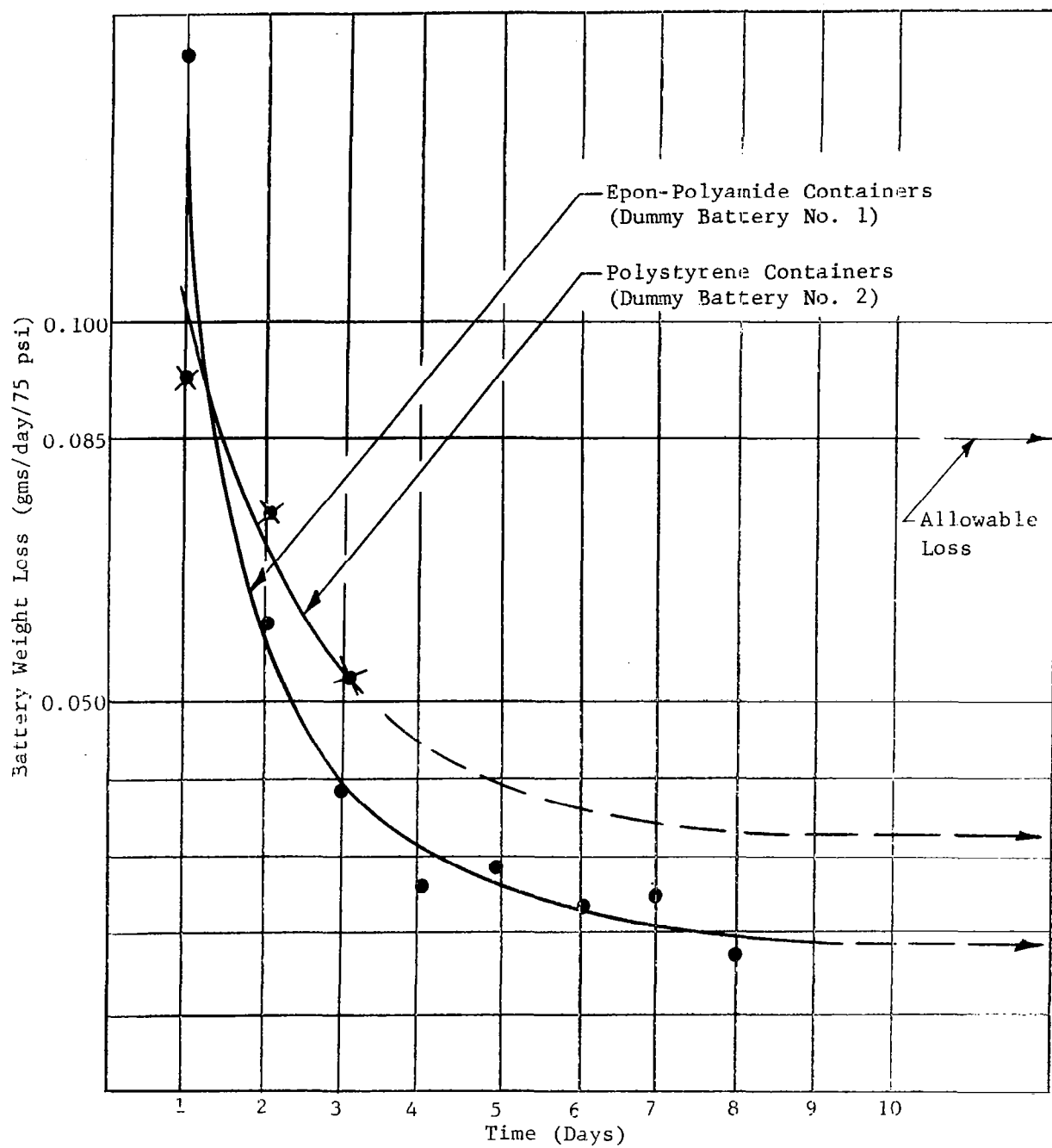


Figure 18. KOH Permeability Test

methods, was 5.57×10^{-5} cc/sec, and after the vibration test it was 7.07×10^{-5} cc/sec. The following additional tests were performed on this battery at Narmco:

1. Freon gas at 50 psi pressure, at room temperature.
2. Freon gas at 150 psi pressure, at 90°F for one hour.

No leakage was detectable in these two tests by the G. E. leak detector with the highest sensitivity.

3. Hydrostatic burst test: The battery was pressurized first to 150 psi and this pressure was held for three minutes. The pressure was then increased to 200 psi and held for three minutes. At pressure over 200 psi it appeared that water leak developed in one cell container and water penetrated between the cells and the wound shell. The pressure was increased to 400 psi and held for three minutes. At that pressure minute water drops formed on the outer surface of the cylinder. The battery failed at 554 psi. It appeared that the failure originated at the area of the cylinder where the water penetrated through the cells.

After burst test, the remaining parts of the battery were inspected and the bond quality between the styrene cells and the wound shell was checked. It revealed that the peel strength was not adequate and explained the separation as observed previously after the low temperature test. This observation justified the bonding tests which were conducted by Narmco's Chemistry Department and which are detailed in Tables XIII through XIX.

Dummy battery number 3 was assembled with dummy electrical leads, using stranded silver and copper wire and following in close approximation the pattern as shown on Power Sources Drawing SK201325. The assembly of the dummy battery is shown on Figure 19. After casting resin over the wires, grinding to 3.00" diameter, and priming with Du Pont's Number 46971/RC-805, the case was wound using the previously established procedures. After cure, the battery was subjected to 75 psi air pressure for five minutes, to 20°C low temperature for three hours, and to additional 75 psi air pressure for five minutes. No leakage or any damage was observed. While setting up the battery for permeability testing with KOH, it was accidentally heated in excess of 250°F. This temperature damaged the styrene material and the battery was scrapped.

TABLE XIII
EXPERIMENT #1

SPECIMEN: 5 mil Teflon FEP, Type 544 bonded to Tyril 767 molded sheet.

TEST: Teflon peeled by hand from the styrene.

STYRENE PREPARATION: 1. Degrease with isopropyl alcohol; 2. dry sand with 400A carborundum paper; 3. Degrease with isopropyl alcohol.

TEFLON PREPARATION: None

CURE CONDITIONS: 48 hours at Room Temperature

Adhesive System	Special Conditions	Test Results And Comments
1. Epon 820/Lancast A, 50/50	None	Fair peel
2. Epon 820/Lancast A, 80/20	None	Good peel - rank #3
3. Epon 828/Versamide 125, 50/50	None	Poor peel - failed to styrene
4. Power Sources Styrene Cement	None	Poor peel - failed to Teflon
5. PolyLite 8037, MEK peroxide (1 phr)	None	Poor peel - failed to Teflon
6. Narmco R & D X-305	None	Very good - rank #1
7. Epon 828/Versamide 125/ Styrene monomer 50/50/5	None	Poor peel - failed to styrene
8. Adiprene L-100, Moca (11 phr)	None	Good peel - rank #4
9. Same as #3	10 min. @ 150°F etch in a bath composed of 30 pts H ₂ O, 10 pts H ₂ SO ₄ , 4 pts Na ₂ Cr ₂ O ₇ distilled H ₂ O rinse, 10 min. @ 180° dry	Good peel - rank #2
10. Same as #3	Primed with styrene monomer, 15 min. air dry	Poor peel - failed to styrene
11. Same as #4	Same as #9	Poor peel - failed to Teflon
12. Same as #4	Same as #10	Poor peel - failed to Teflon

TABLE XIV
EXPERIMENT #2

SPECIMEN: Various Films bonded to Tyril 767 molded sheet

TEST: Film peeled by machine at 180° to styrene sheet

STYRENE PREPARATION: Sand with 400A carborundum paper, degrease with isopropyl alcohol.

FILM PREPARATION: None

CURE CONDITIONS: 4 hours at 125°F

Adhesive System	Film	Special Condition	180° Peel, lbs/in
1. Epon 820/Lancase A, 80/20	Teflon FEP, Type 544, 5 mil	None	3.0
2. Narmco R & D X-305	Same as #1	None	too poor to test
3. Adiprene L-100, Moca (11 phr)	Same as #1	None	10.5
4. Same as #1	Same as #1	Na ₂ Cr ₂ O ₇ etch	8.0
5. PolyLite 8037, MEK peroxide (1 phr)	Saran, 1/2 mil	None	too poor to test
6. Power Sources Styrene Cement	Same as #5	None	too poor to test
7. Same as #1	Same as #5	None	too poor to test
8. Same as #5	Mylar, 5 mil	None	too poor to test

TABLE XV
EXPERIMENT #3

SPECIMEN: 5 mil Teflon FEP, Type 544 bonded to Tyril 767 molded sheet

TEST: Film peeled by machine at 180° to styrene sheet

STYRENE PREPARATION: Sand with 400A carbonundun paper, degrease with isopropyl alcohol

PRIME: Adiprene L-100, Moca (11 phr) brush coated, uncured, or cured 20 minutes at 212°F

FILM PREPARATION: None

CURE CONDITIONS: 4 hours at 125°F

Adhesive System	Prime	180° Peel, lbs/in
1. Epon 820/Lancast A, 80/20	Styrene coated cured	Very good, but could not be tested due to Teflon failure.
2. Epon 820/Lancast A, 80/20	Styrene coated, not cured	3.0
3. Epon 820/Lancast A, 80/20	Teflon coated, cured	5.0
4. Epon 820/Lancast A, 80/20	Teflon coated, not cured	4.5
5. Epon 820/Lancast A, 80/20	Teflon & Styrene coated, cured	6.5
6. Epon 820/Lancast A, 80/20	Teflon & Styrene coated, not cured	9.5

TABLE XVI
EXPERIMENT #4

SPECIMEN: Tyril 767 sheet stock with various resin cast to one surface.

TEST: Tensile shear of 1/2 cut lap section

STYRENE PREPARATION: Sand with 400A carbonundun paper, degrease with isopropyl alcohol.

PRIME: Adiprene L-100, Moca (11 phr) brush coated, uncured, or cured 4 hours at 125°F.

CURE CONDITIONS: 72 hours at room temperature or 24 hours at RT plus 4 hours at 125°F

Casting Resin	Primed	Resin Cure	Room Temperature Tensile Shear	
			Stress, psi*	Failure
1. Epon 828/Versamide 125, 50/50	Yes	Heat cured	712	Styrene sheet
2. Epon 828/Versamide 125, 50/50	No	Heat cured	494	Styrene sheet
3. Epon 828/Versamide 125, 50/50	Yes	RT cured only	580	Styrene sheet
4. Epon 828/Versamide 125, 50/50	No	RT cured only	806	Styrene sheet
5. Epon 820 Lancast A, 50/50	Yes	Heat cured	430	Resin Casting
6. Epon 820 Lancast A, 50/50	No	RT cured only	422	Resin Casting
7. Epon 820 Lancast A, 80/20	Yes	Heat cured	16	Resin Casting
8. Epon 820 Lancast A, 80/20	No	Heat cured	64	Resin Casting
9. Epon 820 Lancast A, 80/20	Yes	RT cured only	50	Resin Casting
10. Epon 820 Lancast A, 80/20	No	RT cured only	44	Resin Casting

*NOTE: No bond failures.

TABLE XVII
EXPERIMENT #5

Experiment #4-1. & 2. repeated with smaller bond area

Casting Resin	Primed	Resin Cure	Bond Area	Room Temperature	
				Tensile Stress, psi	Shear Failure
1. Epon 828/Versamide 125, 50/50	No	Heat cured	.25	188	Styrene sheet
2. Epon 828/Versamide 125, 50/50	Yes	Heat cured	.25	404	Styrene sheet
3. Epon 828/Versamide 125, 50/50	No	Heat cured	.144	1320	Bond shear
4. Epon 828/Versamide 125, 50/50	No	Heat cured	.154	1010	Bond shear
5. Epon 828/Versamide 125, 50/50	Yes	Heat cured	.204	1160	Styrene sheet
6. Epon 828/Versamide 125, 50/50	Yes	Heat cured	.126	1260	Styrene sheet

TABLE XVIII

EXPERIMENT #6

Adhesive System	Primer	Primer Cure	180° Peel, lbs/in	
1. DuPont 46971/RC805	None		5.0	Teflon tear failure
2. DuPont 46971/RC805	THF Saran Soln.	Air dry		Teflon tear failure
3. Epon 820/Lancast A, 80/20	Styrene cement 112-112 glass to styrene	Air cure and sand	4.0	Teflon tear failure
4. Epon 820/Lancast A, 80/20	Toluene diisocyanate	Air dry	2.5	Teflon tear failure
5. Epon 820/Lancast A, 80/20	Formvar 7/70E in methylene chloride	Air dry	4.0	Teflon tear failure
6. Epon 820/Lancast A, 80/20	112-112 glass to styrene with THF	Air dry	No bond, blew due to solvent	
7. Epon 820/Lancast A, 80/20	Acrylonitrile monomer	Air dry	3.5	
8. Epon 820/Lancast A, 80/20	Adiprene L-100, Moca (11 phr)	48 hrs @ RT	6.0	
9. Epon 820/Lancast A, 80/20	Adiprene L-100, Moca (11 phr)	5 hrs @ 180°F	7.0	
10. Epon 820/Lancast A, 80/20	H ₂ SO ₄ Saturated with Na ₂ Cr ₂ O ₇	Water rinse & 180°F Oven dry	6.7	
11. Epon 820/Lancast A, 80/20	Treat styrene with oxidizing flame		5.9	

TABLE XIX

EXPERIMENT #7

SPECIMENS: Styrene to Styrene laps and 5 mil Teflon FEP, Type 544 to Tyril 767 styrene.

TESTS: Room Temperature tensile shear and 180° peel.

SURFACE PREPARATION: Sand the styrene surface with 600W paper, wash with isopropanol to remove loose particles, dry.

SURFACE PRIMING: Apply a thin (1-2 mils dry film thickness) coating of DuPont's #46971/RC-805 adhesive to the styrene surface. Air dry 1/2 hour. Oven dry 10-15 min. at 125-180°F.

BONDING: Coat all adhering surfaces with a thin layer of 80/20, Epon 820/Lancast A adhesive. Assemble adherends and oven cure at 125-180°F for at least 4 hours. The higher the temperature the better for complete cure of the epoxy polyamide adhesive.

DATA

(All tests at RT)

Cured 76 hours at RT		Cured 4 hours at RT and Postcured 72 hours at 125°F	
Tensile Shear	180° Teflon Peel	Tensile Shear	180° Teflon Peel
416	8.8	400*	11.4**
352	8.0	608*	11.5**
357	7.8	960	10.2**
693		432	

*Styrene failure. All other specimens cut for approx. 1/8" overlap.

**Teflon film failed in tear.

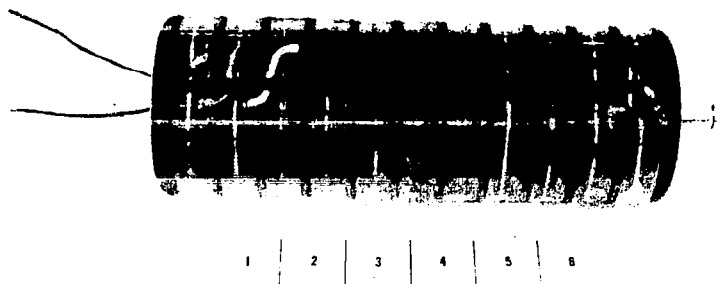


Figure 19. Assembly of Dummy Battery Number 3

As a replacement for dummy battery number 3, Narmco made dummy battery number 4. This battery used styrene cells supplied by Power Sources. It was in every respect identical to number 3, except for the wiring which was done by copper wire only. The case passed all tests to which number 3 was subjected and was given to Narmco's Chemistry Department for permeability testing. The test was similar to those conducted on previous batteries. After a very fast drop of permeability within the first three days, leakage developed which was indicated by a sharp rise of the curve in Figure 20. The battery was removed from the apparatus and inspected. An indicator paper test proved that one copper wire strand at the end plate had traces of alkali and it was assumed that KOH had penetrated between the wires, had attacked the copper and found an exit along the stranded wire. The case was repaired by soldering silver wire strands to the copper wires and by potting the strands in a resin boss.

The permeability test was repeated and the weight loss plotted in the diagram, Figure 20. The losses were under the allowable limit and it is safe to assume that by improved design of the lead outlet, the total permeability of the battery will be very low. The dummy battery number 4 was shipped to Power Sources for vibration and helium leak testing.

After vibration testing, dummy battery number 4 showed signs of delamination of the case from the cell containers. As a result, three more dummy batteries were fabricated for testing. The cases of these batteries were wound over empty cells; no dummy weights were used.

Dummy battery number 5 was primed with Du Pont adhesive 46791/RC-805, as previous batteries, and wrapped with two layers of FEP Teflon tape in the center. The tape thickness was increased toward the ends, making five layers. The resin for applying the tape was Epon 820/Lancast A.

Dummy battery number 6 had no adhesive applied to the cells. Two layers of FEP tape were applied with no adhesive, followed by two layers impregnated with Epon 820/Lancast A.

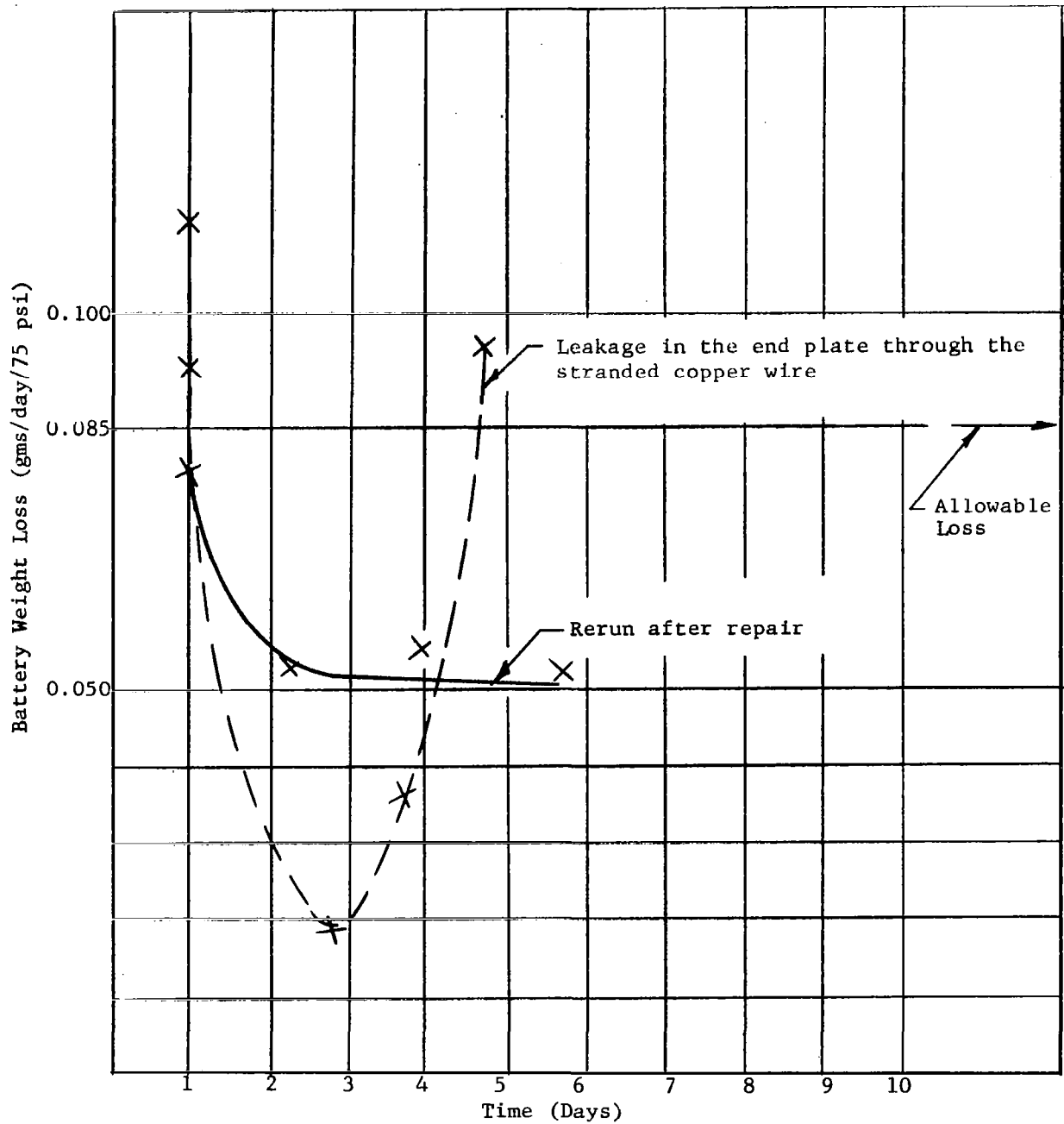


Figure 20. KOH Permeability Test, Dummy Battery No. 4

Dummy battery number 7 was prepared as follows:

1. The surface was primed with Du Pont adhesive 46791/RC-805.
2. One layer of 181-style glass cloth was applied over the cells using styrene monomer to tack it in place.
3. The cloth was impregnated with "Quickset" dental acrylic. Five-mil Mylar was wrapped over this to apply pressure during the cure of 30 minutes at 100°F.
4. The case was then ground down to the glass surface.
5. This surface was primed with Du Pont 46791/RC-805 and two layers of FEP tape, impregnated with Epon 820/Lancast A, were wound on.

The structural winding of dummy batteries 5, 6 and 7 was similar to previous batteries. These batteries were thermally cycled between room temperature and 0°F. Four cycles were applied, each temperature maintained for one hour for each cycle. The batteries were then pressure-cycled to 75 psi at 0°F. They were immersed in an alcohol/dry ice bath maintained at 0°F, and pressurized with gaseous nitrogen. Three cycles were applied, the pressure being held for three minutes on each cycle. None of the batteries showed any signs of leakage during these tests.

After completion of these tests, the batteries were cut and examined. Battery number 5 had some areas of delamination between the FEP tape and the styrene cells. Battery number 6, which had no bond between the tape and cells, showed no signs of damage or delamination. Battery number 7 showed no signs of delamination, and the final fabrication procedure, described in Narmco Process Specification NRPS 1104B (see Appendix B), is based upon a minor modification of the procedure utilized in the fabrication of this battery.

III. SUMMARY AND CONCLUSIONS

The major problems encountered in this program were a result of material incompatibility. The only material for the cell containers which met the permeability requirements and was resistant to a KOH solution was styrene. This, in turn, was not compatible with the epoxy polyamide resin used in applying the FEP Teflon film leakage barrier and the filament wound structural case.

This program showed, however, that by logical engineering and process applications, these problems could be solved, and the result was a lightweight, reliable, high cycle life battery for space applications. All work performed on this program utilized existing materials and present state-of-the-art processes.

PHASE II - ELECTROCHEMICAL DESIGN

IV. INTRODUCTION

The original concept of the duplex, or bipolar plate for the battery construction was studied early in this phase of the program. The solutions of the problems presented by this type of construction were felt to be outside of the scope of the program. Therefore, it was decided to continue the project on the basis of evaluating more conventional types of electrode structures. From the results of these studies, prototype cells were built and tested, and their designs were then translated to the Phase III effort.

BIPOLAR PLATE STUDIES

A. Basic Electrode Fabrication and Study of Active Material Properties

Several methods of plate fabrication were performed. The first test cell (cell A) was constructed using a pasted plate. The pasted method of application using a paste mixture composed of chemically prepared silver (II) oxide and carboxymethyl-cellulose binder produced an uncontrollable paste which slumped and ran under the pasting mask. Likewise, the negative material made by the same method, exhibited the same characteristics. Both mixes were pasted on opposite faces of a common silver foil collector.

An alternate technique which was more easily controlled employed the use of chemically prepared silver (II) oxide applied to the foil in powder form within the pasting mask. After the material was uniformly spread over the active area, a few drops of 2% polyvinyl alcohol binder were added to the powder and allowed to soak in, binding the material. On the reverse side of the foil, cadmium powder was similarly bonded. This method of duplex plate fabrication was evaluated in cell B.

The use of a sintered and formed plaque based on monovalent silver oxide and binder was unacceptable because of oxidation of the exposed foil area during formation of the active material to silver (II) oxide.

The sintered, resin bonded technique of active material application was acceptable. In this method a sheet of resin bonded silver powder, cut to the appropriate size and shape, was placed on the foil and heat bonded in place. The electrode was then placed in a sintering furnace and the resin burned out of silver. After cooling, cadmium hydroxide powder was bonded to the reverse side with PVA, as described above (see cell B). This type of electrode was used in the third test cell, cell C.

At this point, a technique was developed that allowed construction of duplex, or bipolar, plates in either the dry charged or dry discharged state. Plates of both types had the required

degree of structural integrity necessary for handling during assembly of cells. For dry charged plates, a circular piece of expanded silver foil was spot welded to each side of the foil collector. The active material thus filled the voids in and around the strands which served to lock the material to the solid foil collector. For a dry discharged plate, the same method was used to prepare the negative side. However, the positive side was prepared with resin bonded silver sintered directly to the foil without the expanded metal reinforcement. The active negative material was cadmium hydroxide to which had been added small percentages of cadmium metal and silver powders.

An additional test cell was constructed similar to cell A, using the dry charged type of construction described above. The main difference was that, whereas cells A through C had been three plate cells, this cell, cell D, consisted of two plates. This was done to study the effect of spacing, quantity of electrolyte, and action of the active electrode materials.

Cell E was constructed to test the self-discharge of a duplex plate using silver foil as a base material. A duplex plate was made with the active materials -- cadmium powder and divalent silver oxide -- applied as a circle in the center of each side circular piece of 0.0015" silver foil. The plate was mounted between Lucite blocks and sealed with two concentric O-rings on each side of the active plate. The space between the plate and the plastic on each side was filled with electrolyte, the fill holes sealed, and the cell allowed to stand to observe any action of self-discharge.

Cell F was similar to cell E, except that platinum foil was used in place of silver foil.

Cells A through F were built to study the duplex plate. The constructions, along with test results, are summarized in Table XX. Subsequent constructions evaluated more conventional plate designs.

The test cell fixtures for the duplex plate studies were built of 0.5 inch Lucite plates six inches square. Bolt holes were drilled in each plate in a circular pattern outside of the gasket area for clamping the cell together. This fixture allowed a

TABLE XX
BIPOLAR PLATE CELLS

<u>Cell</u>	<u>Positive Electrode</u>	<u>Negative Electrode</u>	<u>Separator</u>	<u>Test Results</u>
A	AgO 2% CMC	Cd powder 5% Ag ₂ O 2% CMC	1 - EM 341 6 - 300 PUD- O 6 - EM 341	Electrolyte leak paths between gaskets and plates. Cell scrapped.
B	AgO 5% Ag 2% PVA	Cd powder 5% Ag ₂ O 2% PVA		High IR. Space of elec- trodes too great. Cell scrapped
C	Ag (RB sintered)	Cd(OH) ₂ 5% Ag PVA	1 - EM 341 4 - 300 PUD-O 4 - EM 341	Maximum discharge - 40 minutes at 250 ma. Bi- polar plate not charged.
D	AgO 2% CMC	Cd powder 5% 5 Ag 2% CMC	1 - EM 341 4 - 200 PUD-O 4 - EM 341	Discharge 1 A for short time. Variability of electrode spacing
E	AgO	Cd powder	-	To check self discharge. O ⁼ migration.
F	AgO / Pt / Cd powder			No O ⁼ migration, but AgO → Ag ₂ O

large gasket sealing area while maintaining appropriate diameters for the electrodes and separators. The fixtures were preassembled with gaskets, and were pressure tested at 150 psig to verify their ability to withstand leakage.

Concurrently with the duplex plate activity, a separator evaluation program was being performed. Since the results of this program were not available at this time, separators used in the duplex plate evaluation consisted of non-woven dynel wicks, plus cellophane.

B. Test Results

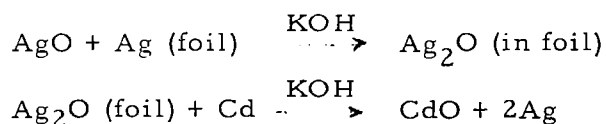
Cell A: This cell exhibited several electrolyte leak paths, apparently between gaskets and electrodes before any electrical cycles could be run. The cell was taken apart and examined. It was determined that the gasket-electrode and the gasket-cell case interfaces did not provide an adequate seal against the electrolyte.

Cell B: This cell exhibited high internal resistance on charge and discharge, and consequently very poor voltage response. The poor performance was initially attributed to a deficiency of electrolyte. The cell was then disassembled, electrolyte added, and was then reassembled. Further attempts at discharging yielded only marginal performance. The cell was again taken apart and a critical analysis made. The conclusion was that the space between the electrodes was too great.

Cell C: Performance of the cell was unsatisfactory. After an initial wet stand, the cell was placed on charge. The initial charge acceptance was good; however, the discharge capacity was very poor, even at very low current density discharges. Additional electrolyte was introduced into the cell without appreciable improvement in performance. The maximum discharge capacity was 40 minutes at 250 milliamperes. The cell was taken apart and examined. It was found that the outside plates -- one positive and one negative -- were properly charged, but that the bipolar plate -- the center plate -- was in the discharged condition. No electrolyte could be detected around the edge of the foil collector. On the outside positive plate collector, the area covered by the positive material had small areas which had been converted to silver oxide. This indicated that there had been silver oxide formed in the silver collector.

Cell D: Initial attempts to cycle the cell at 100 milliamperes indicated a very high internal resistance. After several days' wet stand, the internal resistance had decreased from approximately 12 ohms to about 3 ohms. During this time, the cell had been in a position such that the plates were on a horizontal plane. When placed vertically, the internal resistance dropped to where discharge currents as high as one ampere could be sustained for a short period of time. However, this cell developed only a small fraction of the capacity of conventional plates with equivalent amounts of active material.

Cell E: Initial reaction between divalent silver oxide and the foil was observed. The exposed areas of the silver foil in contact with electrolyte became dark, indicating that reaction was proceeding. After two weeks, the formation of dark spots on exposed silver areas of the negative side, and the formation of a light pink area of cadmium oxide were evident. This indicated that oxygen transport had occurred through the silver foil. Subsequently, it was found that reduction of the silver oxide to free silver had occurred at the interface between the foil and the silver oxide. Oxidation of cadmium to cadmium hydroxide had occurred at sites opposite to those areas of maximum silver oxide reduction. Analysis of the silver oxide for Ag₂O content indicated that a 20% reduction in capacity had occurred. This did not take into account the layer which had been reduced to free silver. Determination of the cadmium material indicated that a similar change had occurred. The results indicate confirmation of the possible series of reactions:



The formation of Ag₂O in the foil may be postulated as being formed throughout -- with a possible concentration gradient -- by means of solid state oxygen ion migration. This is suggested by the work of Dirkse.¹

Cell F: Analysis of this cell (platinum foil) indicated no effect such as reported for cell E other than normal decomposition of the divalent silver oxide to monovalent oxide in alkaline solution.

¹ J. Electrochem. Soc. 107, 859 (1960).

Table XX is a summation of construction data and test results of bipolar plate cells.

The imposing problems presented by the bipolar plate study are: (1) the inability of the bipolar plate to accept recharge, and; (2) the apparent high degree of self discharge of the plate due to corrosion of the foil. Other problem areas are: The low efficiency of material utilization; the difficulty of electrolyte addition; the extremely tight tolerances required put fabrication beyond normal manufacturing procedures.

VI. CELL REDESIGN

Upon consideration of the above problems, a critical review of the proposed design was made. It was found that an alternate design consideration was possible that could fulfill the basic requirements and alleviate many of the difficulties encountered or anticipated in the proposed bipolar plate design. Basically, the proposed design change would involve the development of a round cell of more conventional design, but with anticipated full battery capacity. These cells would then be connected in series to give the desired battery voltage, i. e., the individual plates would be paralleled within a unit cell to give total capacity, then the cells would be series connected to give battery voltage. It was originally planned to build a monoblock of the ultimate battery voltage, then to parallel the monoblocks for the desired capacity.

The initial test cell design is illustrated in Figure 22. A comparison of the two designs is made in Table XXI. The "conventional" plate design allowed for unit cell testing, as well as for adjustment of the relative state of charge between individual cells prior to final battery assembly.

TABLE XXI
COMPARISON OF CELL DESIGNS

	Design 1 Bipolar Plate	Design 2 Conventional Plate
Total Cells per Battery	110	11
Cells per Monoblock	11	-
Monoblocks per Battery	10	-
Unit Cell Capacity, AH	1	10
Plates per Cell	2	13
Metal to Plastic Seal		
Linear inches/cell (A)	18.6	1.08
Linear inches/battery	2046	11.88
Leak path between adjacent cells (B), inch	0.50	1.3
Leak ratio per cell - A/B	37.2	0.83
Electrolyte Addition Points	220	11
Variation in Cell Fit, per Positive Plate, due to Tolerances - Percent	16	1

NASA EXPERIMENTAL CELL

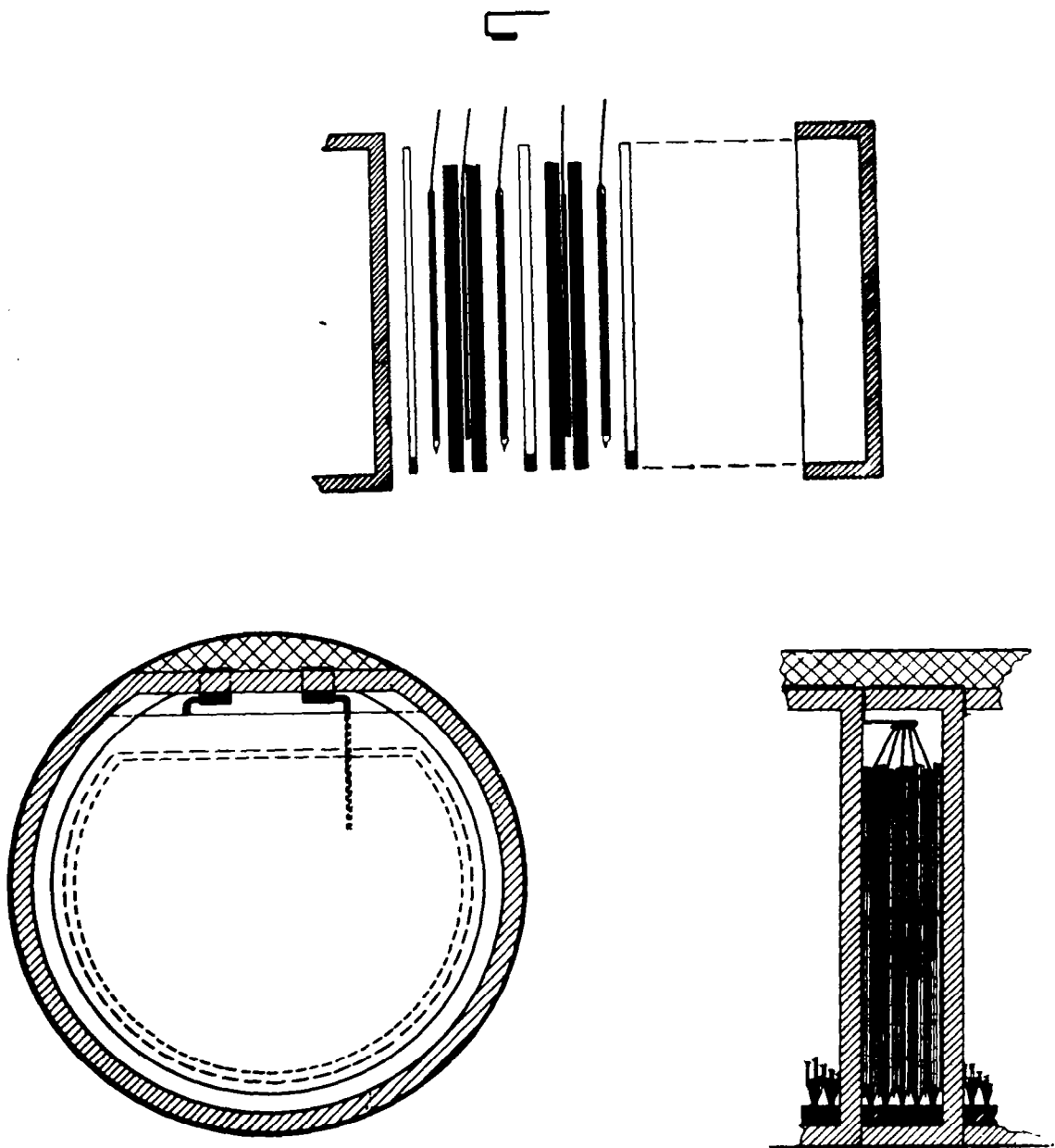


FIGURE 22

A. Preliminary Electrode Studies

Electrodes for the silver oxide-cadmium system can be manufactured by a variety of methods as disclosed in the available literature on the subject. Prior experience at Power Sources Division was an important factor in deciding on the course of the preliminary investigation of the plate type and composition. In the choice of the type of silver electrode, there was an ample backlog of manufacturing experience. The choice of types was made on the basis of the initial condition of the plates, namely a composition corresponding to the charged or discharged states of the active material. In the case of the negative cadmium plate, the orientation of the thinking was in terms of the pasted type of plate which was an approach in line with the available manufacturing procedures in the plant. It was therefore most important to establish that negative plates having the required coherency and strength would result for the required cycling conditions. This point of view led automatically to the three-plate cell with a single negative electrode as the testing medium. The high lights of the materials and processes are presented in the following descriptions.

1. Positive Plate: Of the variety of methods that have been proposed and used for the preparation and manufacture of silver plates, manufacturing procedures utilize the pasted type in which the active material is applied in the state of charge desired on assembly of the cell and the sintered type in which silver or a thermally decomposable silver salt or oxide is shaped in the form of a plate and is then heated to produce a coherent and porous silver body, usually containing an imbedded grid or collector. In the sintered type plate, the electrode as made contains silver in the metallic state corresponding to the fully discharged state. It may be used in this state for the cell assembly or may be formed by anodic oxidation in alkaline electrolyte to convert the silver to the oxide form at the state of charge that is desired.

- a. Pasted plate; silver (II) oxide active material: Chemically precipitated AgO is made into a paste with water containing a suitable binder, carboxymethyl cellulose in the present case and having a viscosity suitable to the manner of application. The paste is applied mechanically to both sides of etched silver foil, 0.011 inch in thickness. The initial layer is allowed to air dry 15 to 20 minutes prior to application of the paste to the reverse side of the foil strip. The final thickness and weight is determined, and the material put in desiccated storage. From these strips, plates are cut to the proper size and tabs are attached. These plates are used in the cells assembled with active materials in the charged form. It was deemed important to determine the stability of this type of construction on cycling since the mode represents an easily controllable means where the design requires the active materials to be in the charged state on assembly.
- b. Sintered plate; silver metal powder: Finely divided silver powder and an inert thermoplastic binder, polyethylene in this case, is milled under careful temperature control to obtain a uniform dispersion. The mixture is rolled into thin sheets of the desired thickness. These sheets are then applied by pressing to an expanded silver metal foil grid. During the sintering operation, the resin is burned off completely while the silver particles are bonded to form a porous matrix and to the silver grid. The strip may be rolled to the desired thickness. In the manufacturing operation, strips are coined to the outline of the plate and for attachment of tabs. If used in the manufactured and unformed state, they are cut to size and tabs are attached. If the plate is to be used in the formed and charged stage, the strips are formed after coining and attaching tabs and are usually cut after the formation. In the preliminary program, the plates were used without formation.

All positive plates used during this investigation were made in the plant facilities.

2. Negative Plate: From a general point of view, the secondary battery plate may be considered as consisting of four parts, namely active material consisting of the electrochemically active system, the carrier of varying form such as envelopes of perforated metal or porous metal, the grid or support, and the lead. These functions are often combined, always with the object of minimizing weight, improving performance, and simplifying the manufacturing operation. The pasted plate type, combining the active material and carrier functions, offers the quickest route to minimum weight and ease of manufacture if the active materials have the proper electrochemical activity and have the property of forming a coherent, electronically conductive mass.

The pasted type of plate was within the scope of the type of manufacturing operation carried out in the regular production practice. Experiments had indicated the feasibility of obtaining the desired properties with a finely divided cadmium powder which is manufactured by vacuum cooling of vaporized metal. It was decided to supplement this material with hydroxide, thus enabling the preparation of plates with the cadmium present as metal as in the charged plate and with cadmium present in the oxidized state as in the discharged condition of the plate. Further details are presented in the following paragraphs.

- a. Pasted plate; cadmium powder. No known successful use of metallic cadmium powder for manufacturing negative plates has been reported. The finely-divided cadmium powder manufactured by electrolytic procedure for the pocket type of nickel-cadmium battery is in reality a cadmium-iron powder which is oxidized before using it as active material. For the present work there was used an ultra-fine cadmium powder in which the particle size was 98% by weight less than 15 microns.

This powder was made up into a paste with an aqueous solution of polyvinyl alcohol as the binder. Expanded metal grids cut to size were coated by dip pasting. For the present series of experiments, mixtures of the cadmium powder were made and in particular the effect of the addition of silver (I) oxide was studied. It had been noted in the earlier work that silver oxide behaved as an extender in the pasted cadmium plate.

- b. Pasted plate; cadmium hydroxide: The possibility of the need of adjustment of the state of charge of a battery plate in relation to the state of charge of the opposite electrode suggested the need for experimenting with mixtures of active material in which the cadmium was present mainly in the oxidized state. It was decided to start with cadmium hydroxide, the chemical composition of the cadmium in the discharged state of the electrode. For these tests, the cadmium hydroxide was prepared by dissolving cadmium metal powder of high purity in C.P. nitric acid, evaporating repeatedly to remove excess acid, and precipitating the cadmium hydroxide. The cadmium hydroxide was washed with water to remove soluble nitrates.

A total of eight cell groups was made up using eight compositions of active materials for the negative plates and using two types of positive plates. The plan of the experimentation is summarized on Table XXII.

Each cell group consisted of three cells representing replicate construction with two positive plates and one negative plate. The element was assembled in a suitable plastic container with the vent covered with sealing tape after addition of sufficient electrolyte with the level just above the bottom of the plates. Shims were added to the element wherever the fit inside the container was deemed to be loose. The basic construction and data are shown in Table XXIII.

TABLE XXII

PLAN OF EXPERIMENTATION
GROUPS N-I THROUGH N-VIII

No.	Negative Active Material			Positive Plate Type	
	CD	Cd (OH) ₂	Ag ₂ O	Pasted	Sintered
	Per Cent	by Weight	-----	AgO	Ag
N-I	100	0	0	X	-
N-II	90	10	0	X	-
N-III	95	0	5	X	-
N-IV	85	10	5	X	-
N-V	0	100	0	-	X
N-VI	25	75	0	-	X
N-VII	0	95	5	-	X
N-VIII	25	70	5	-	X

TABLE XXIII
CONSTRUCTION DATA
GROUPS N-I THROUGH N-VIII

Negative plates, number	1
Positive plates, number	2
Separator system (+ to -)	
layer	1 EM 341 Non-woven dyne1
layer	4 PUDO-300 Cellophane
layer	1 EM 341 Non-woven dyne1
Plate area, per side, sq. in.	2.625
Electrolyte, KOH concentration	45% by weight

	Negative	<u>Plate Weights & Thicknesses</u>		Positive		
	Average of 3			Average of 6		
Group No.	Weight grams	Thickness mils	Unit Wt. mg/mil	Weight grams	Thickness mils	Unit Wt. mg/mil
N-I	5.712	28.1	203	3.933	25.4	155
N-II	5.843	29.0	201	3.360	28.7	117
N-III	5.041	27.7	182	3.769	31.6	119
N-IV	4.818	24.8	194	3.402	28.0	121
N-V	1.918	29.0	66	3.069	14.3	214
N-VI	3.017	29.3	103	4.347	17.8	244
N-VII	2.493	27.4	91	4.293	18.8	228
N-VIII	2.864	27.1	106	3.020	13.8	219

In testing the cells, those of Groups N-I through N-IV having been assembled with AgO pasted positives, were given a brief formation charge in order to provide active surface on the negative plate active material which as assembled consisted mainly of metallic cadmium. This initial charge was followed by cycles with two manually controlled discharges to the knee of the curve. The cells of Groups N-V through N-VIII were subjected to the normal formation charge based on the silver plates and this charge was followed by two full discharge cycles.

All cells were then placed on automatic cycling, with the exception of Groups N-I and N-II, which as may be seen from Table XXIV showed low capacities on the manual capacity test, compared to those obtained for the corresponding cells, Groups N-III and N-IV. The automatic cycle consisted of a 60-minute charge at 100 ma and a 30-minute discharge at 200 ma, or input and output being set equal to six amp-minutes. The results of the tests are summarized in Table XXIV.

At the time of removal of any cell from the circuit and completion of the testing for those cells, it was found on examination that all failures were the result of corrosion of the solder connections between the plate tabs and the terminals. It had not been anticipated that only small differences in performance would be found during the early cycles and no protection of the connections was provided in the design. On reviewing these results it is not improbable that the cycling rates were selected at too low a level in comparison to the capacities of the cell groups.

From the performance data of these cells, four of the construction types, two from the first group N-I to N-IV and two from the second group N-V to N-VIII were selected as the basis of design for the larger cell next to be studied. These constructions were those corresponding to Groups N-III, N-IV, N-VI and N-VIII.

TABLE XXIV

NEGATIVE TEST CELL PERFORMANCE

List of Symbols:

G = Good

P = Poor

F = Fair

VP = Very Poor

Group	Capacity (Minutes)		Max. Cycles	Final Conditions				Membrane Separator	Neg. Sep.	Pos. Sep.
	Cyc. 1	Cyc. 2		Neg. Plate	Pos. Plate	Neg. Term.	Pos. Term.			
<u>N-I</u>										
Cell 1	X	X	2							
Cell 2	13	14	2							
Cell 3	21	26	2							
Cell 1 initial short, group not cycled										
<u>N-II</u>										
Cell 1	23	26	2							
Cell 2	29	34	2							
Cell 3	29	X	2							
Group not cycled										
<u>N-III</u>										
Cell 1	37	47	386	G	G	VP	F	G	G	G
Cell 2	42	52	386	G	G	P	P	G	G	G
Cell 3	38	50	386	G	G	P	F	G	G	G

TABLE XXIV (continued)

Group	Capacity (Minutes)		Max. Cycles	Final Conditions						
	Cyc. 1	Cyc. 2		Neg. Plate	Pos. Plate	Neg. Term.	Pos. Term.	Membrane Separator	Neg. Sep.	Pos. Sep.
<u>N-IV</u>										
Cell 1	26	34	386	G	G	VP	F	F	G	G
Cell 2	26	33	386	G	G	VP	F	F	G	G
Cell 3	36	45	386	G	G	VP	G	F	G	G
Reduced voltage after 365 cycles										
<u>N-V</u>										
Cell 1	27	26	94	G	G	P	F	G	G	G
Cell 2	27	23	62	G	G	F	F	G	G	G
Cell 3	29	26	95	G	G	F	F	G	G	G
<u>N-VI</u>										
Cell 1	51	45	386	G	G	VP	F	G	G	G
Cell 2	53	47	386	G	G	P	G	G	G	G
Cell 3	49	47	386	G	G	P	F	G	G	G
<u>N-VII</u>										
Cell 1	41	34	127	G	G	P	P	G	G	G
Cell 2	48	44	127	G	G	P	P	G	G	G
Cell 3	44	42	386	G	G	P	F	G	G	G
<u>N-VIII</u>										
Cell 1	42	40	386	G	G	P	F	G	G	G
Cell 2	34	32	16	G	G	P	F	G	G	G
Cell 3	35	31	386	G	G	P	F	G	G	G

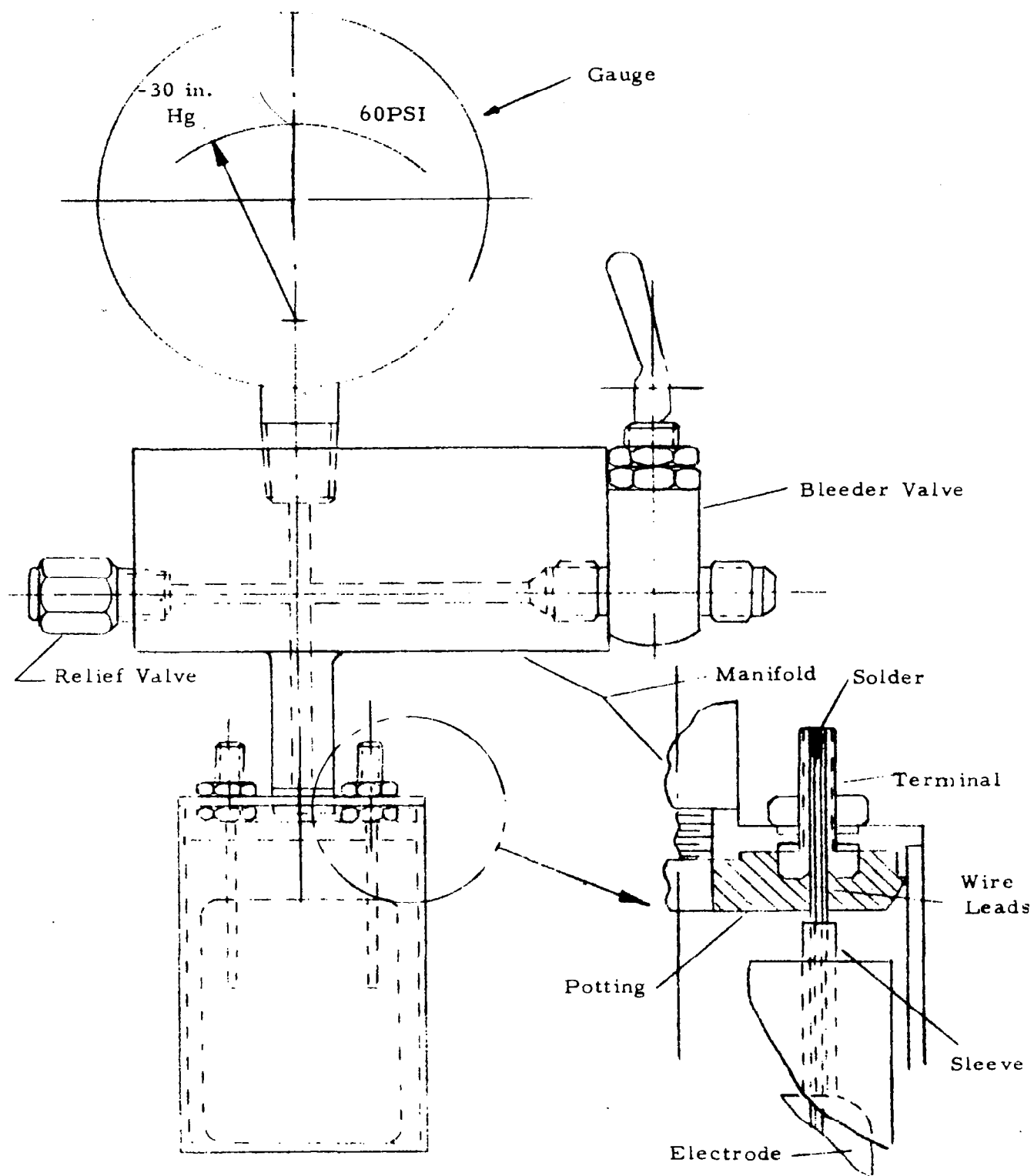
B. Test Cell Design

To further facilitate plate and cell development, four of the plate constructions and plate combinations which looked promising under the preliminary investigations were selected for translation to the design of larger cells. In these cells, the balance of plate group capacities could be brought into closer approximation to practical design requirements and closer attention was imposed with regard to the details of cell construction such as the fit of the element, electrolyte volume, and similar considerations of cell design and manufacture which are important for prolonged cycle operating conditions. It was expected that the cell design would lead to the desired confirmation of the mechanical stability of the plates under cycling conditions, with particular emphasis on the negative plates, and to indications on balance of plate group capacities for operation in the sealed condition. It was estimated that the basic cell design would result in capacities between two and three ampere-hours. The actual capacity would be determined by the amounts of active materials and their coefficients of utilization as modified by the design condition of limited electrolyte and by operating conditions such as charge acceptance and temperature.

Each cell group was made up of five replicate cells. Provision was made to fit one cell in each group with a pressure gauge. The remaining four cells of each group were simply stoppered with a molded PVC vent cap with Bunsen type valve slits. The construction of the test fixture of these cells is illustrated in Figure 23. The construction of all cells was identical with the exception of the active materials of the plates. . . Pertinent details have been summarized in Table XXV.

After assembly of the cells and addition of electrolyte, the cells were given four manual cycles following the course of the formation cycles applied to cells of the preliminary studies. The cells were then placed on automatic cycle providing for manual adjustment of the discharge current on any particular cycle to the desired level. The cycle consisted of a discharge for 35 minutes at various rates and a charge for 55 minutes at a constant potential of 1.6 volts per cell with the maximum current limited to 5.0 amperes per cell. After a number of cycles, the cells were "balanced" by connecting the cells of

FIGURE 23 - Typical Construction of Test Cell



each group in parallel and subjecting them to a constant potential charge at 1.6 volts per cell with a maximum initial charging current of one ampere per cell. The charge was continued until the charging current had dropped to about fifty milliamperes per cell. The electrolyte levels were then adjusted. The cell of each group that was provided with the pressure gauge was sealed after reducing the pressure of each cell to -10 psig. These gauge-equipped cells had been completely potted in a polyester resin and checked for gas leakage prior to the final sealing by using the helium leak detector. The automatic cycling was then continued. The voltages at the start and end of discharge, the discharge rate, and the cell pressures are plotted for each group in Figures 24, 25, 26 and 27.

Severe difficulties were encountered with the maintenance and regulation of the power supply within the automatic cycling equipment during the testing. The malfunction of the equipment caused either severe overdischarge or overcharge of the test cells on a number of occasions. It is difficult to estimate the damage to the life cycling capabilities of the cells because of the malfunctions of the equipment. However, the malfunctions afforded opportunities to note the nature of the gas evolution and recombination which occurred in the sealed cells (with the pressure gauges) under the severe conditions that the malfunction imposed. Several times the cell voltage exceeded the preset limit of 1.6 volts and went as high as 1.9 volts during the charge. During the high voltage charge, the pressures increased but subsequently with readjustment of the cycling conditions the pressures dropped to low levels. Similar effects were noted after the malfunction of the equipment subjected the cells to overdischarge. Negative voltages were found indicating that all cells had been reversed with accompanying gas evolution. Here again, the pressure was found to decrease to the average operating level after the proper cycling conditions were restored.

Overcharge would be expected to result in hydrogen evolution for the cells in Groups N-XI and N-XII; overdischarge for a sufficient time period would bring about hydrogen evolution on the positive plates. Since the pressures on overcharge did not increase to exceedingly high values, it must be assumed that the hydrogen gas was oxidized at the silver electrodes at an appreciable rate. This re-oxidation must also be

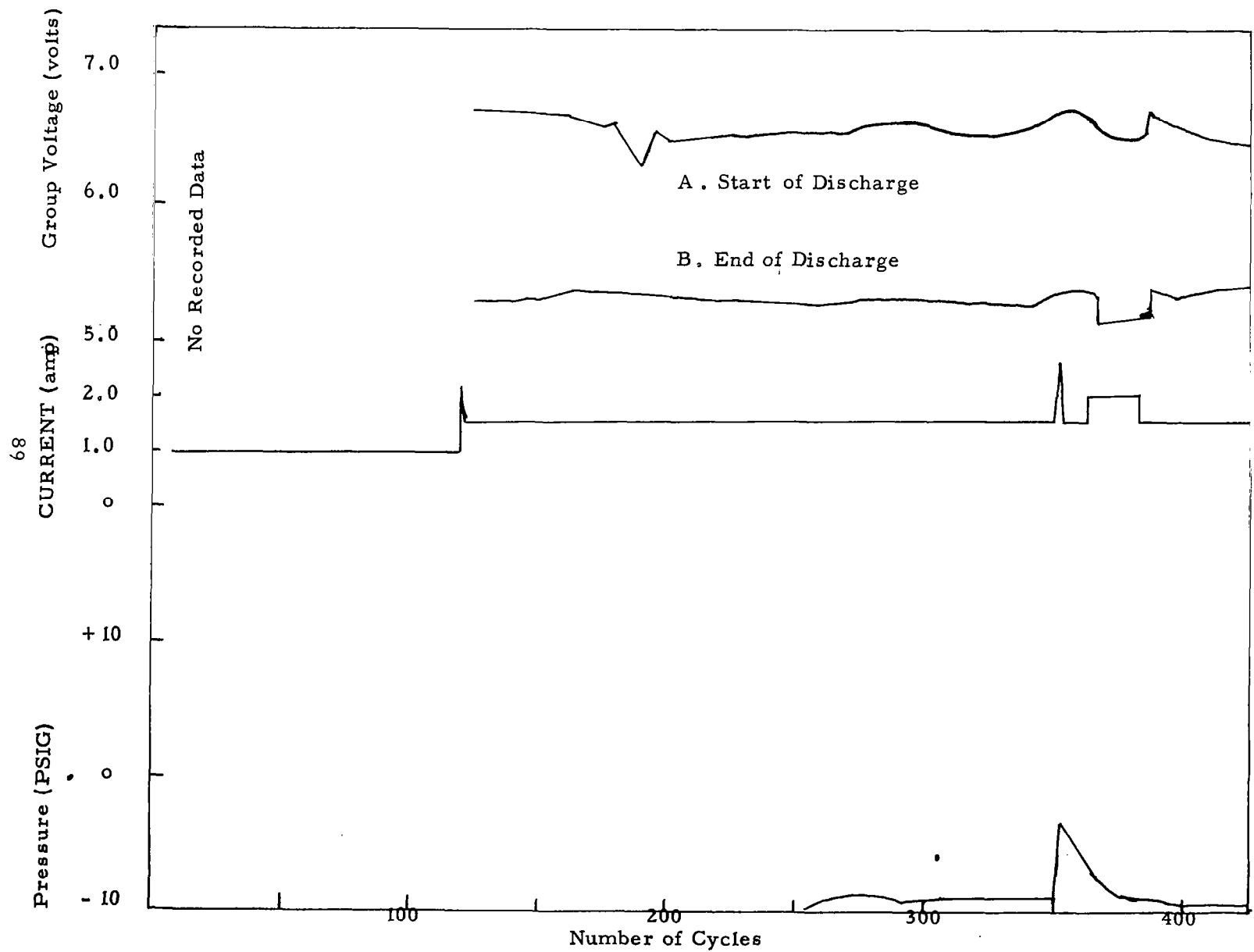


Figure 24 Plot of Electrical Performance of Group N-IX (5 cells) vs. Number of Cycles

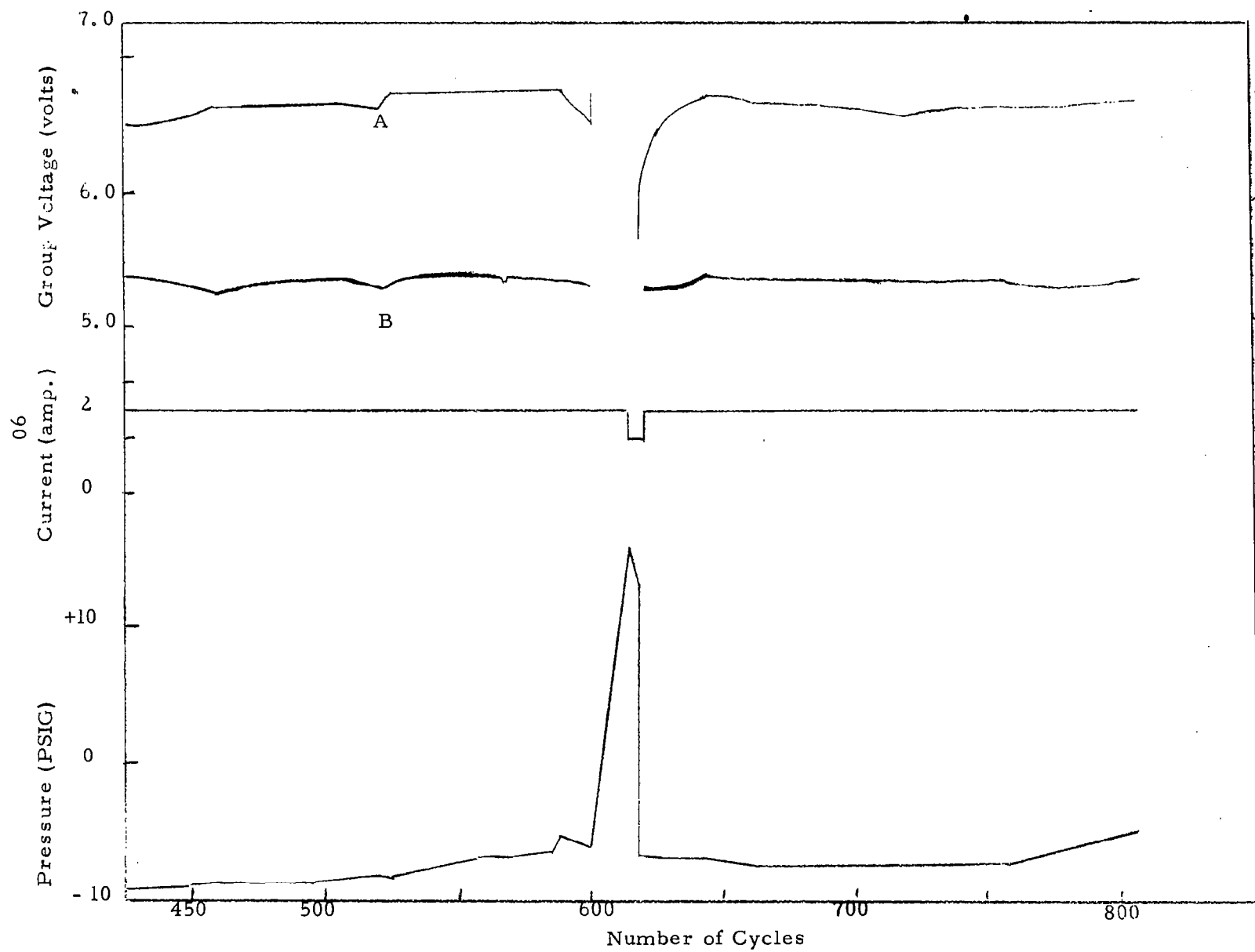


FIGURE 24 (Continued)

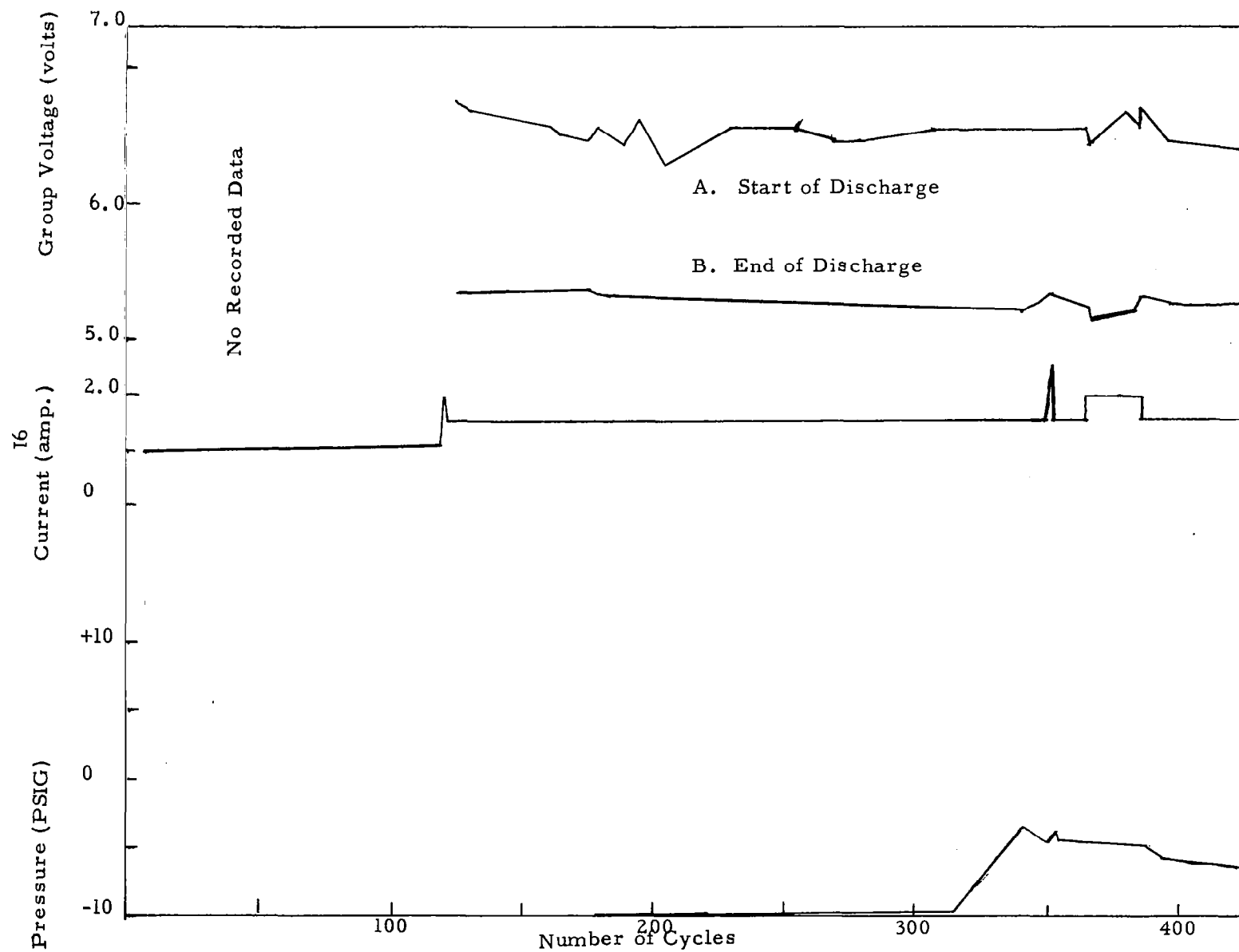


FIGURE 25 Plot of Electrical Performance of Group N-X (5 cells) vs. Number of Cycles

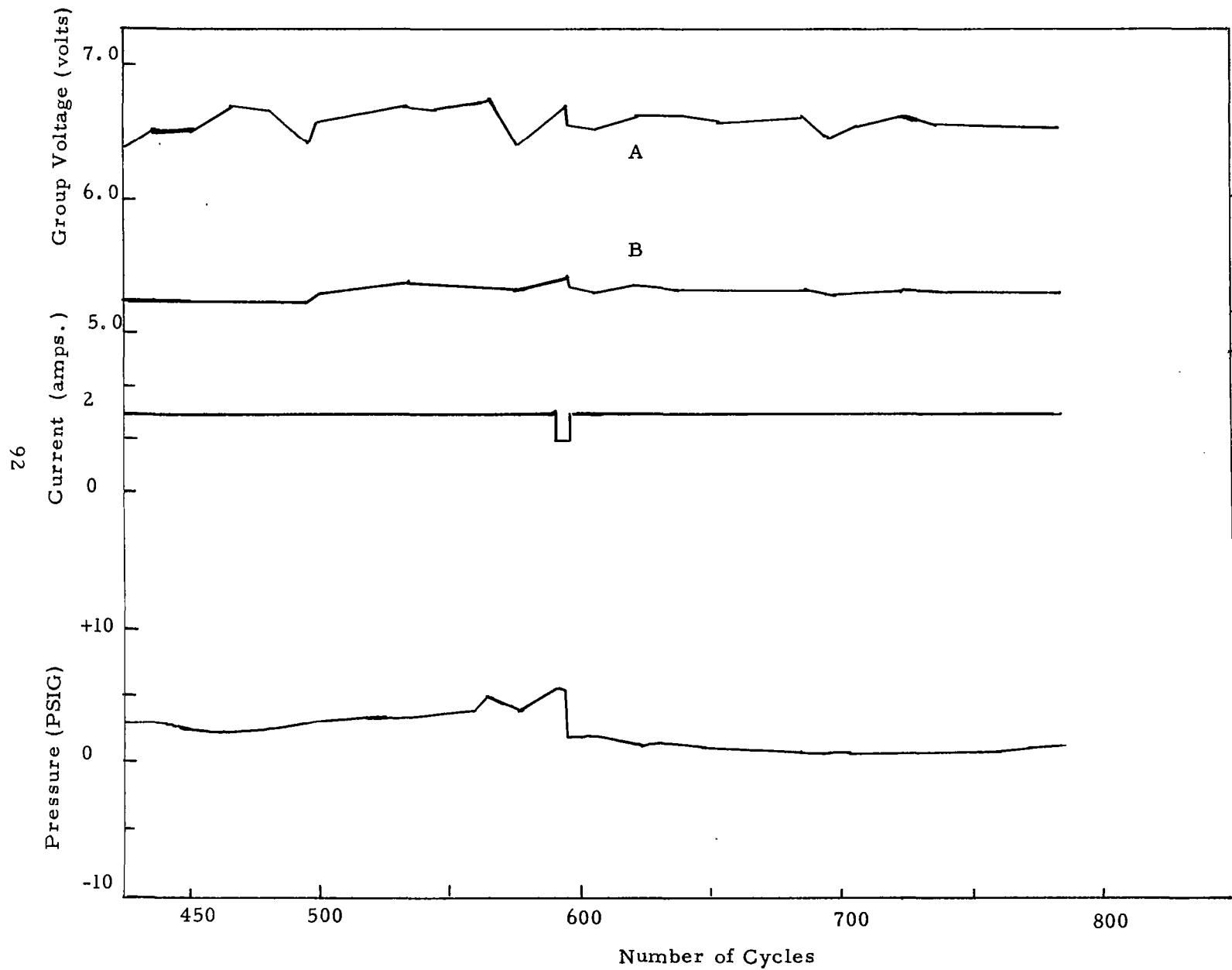
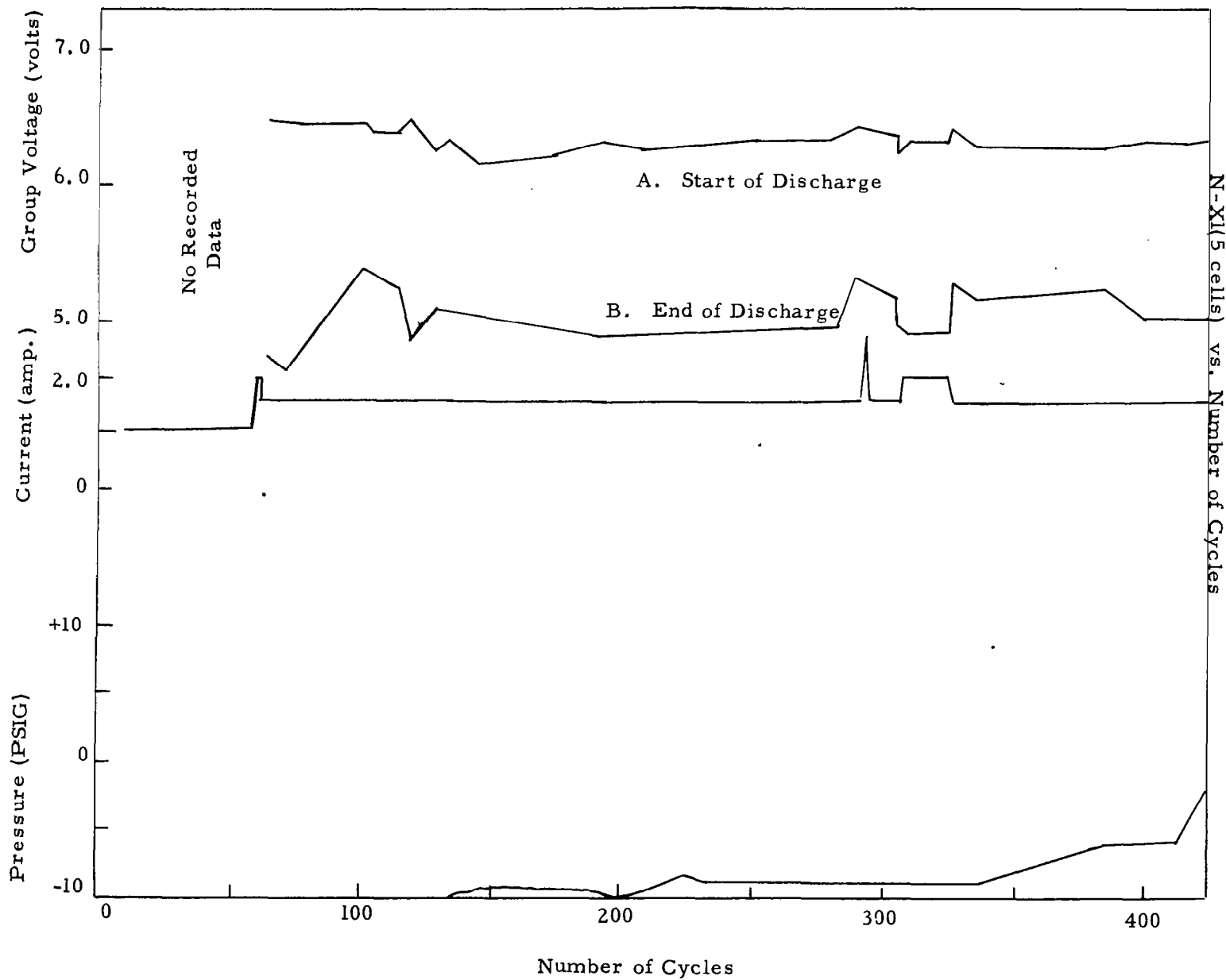


FIGURE 25 (Continued)



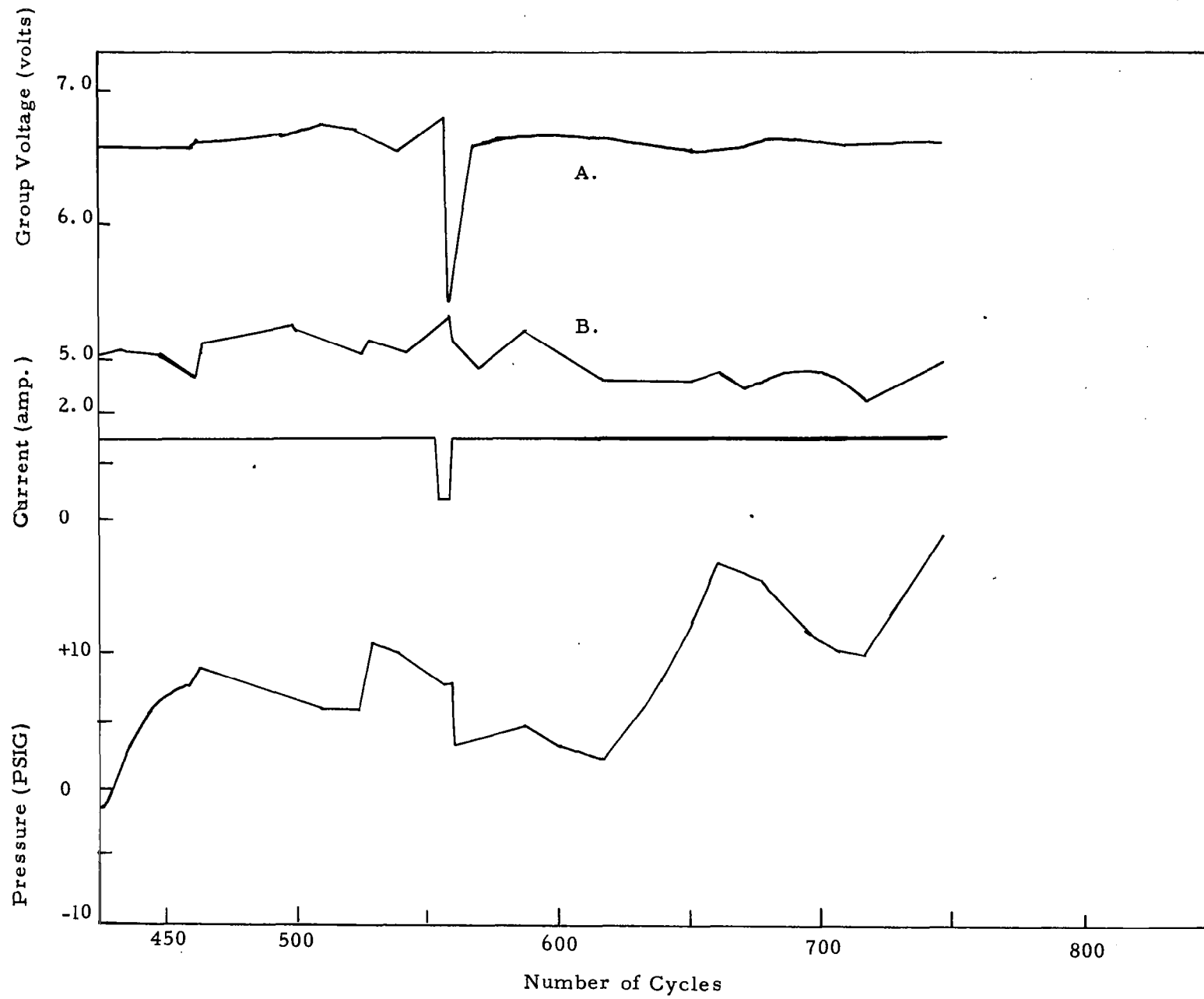


FIGURE 26 (Continued)

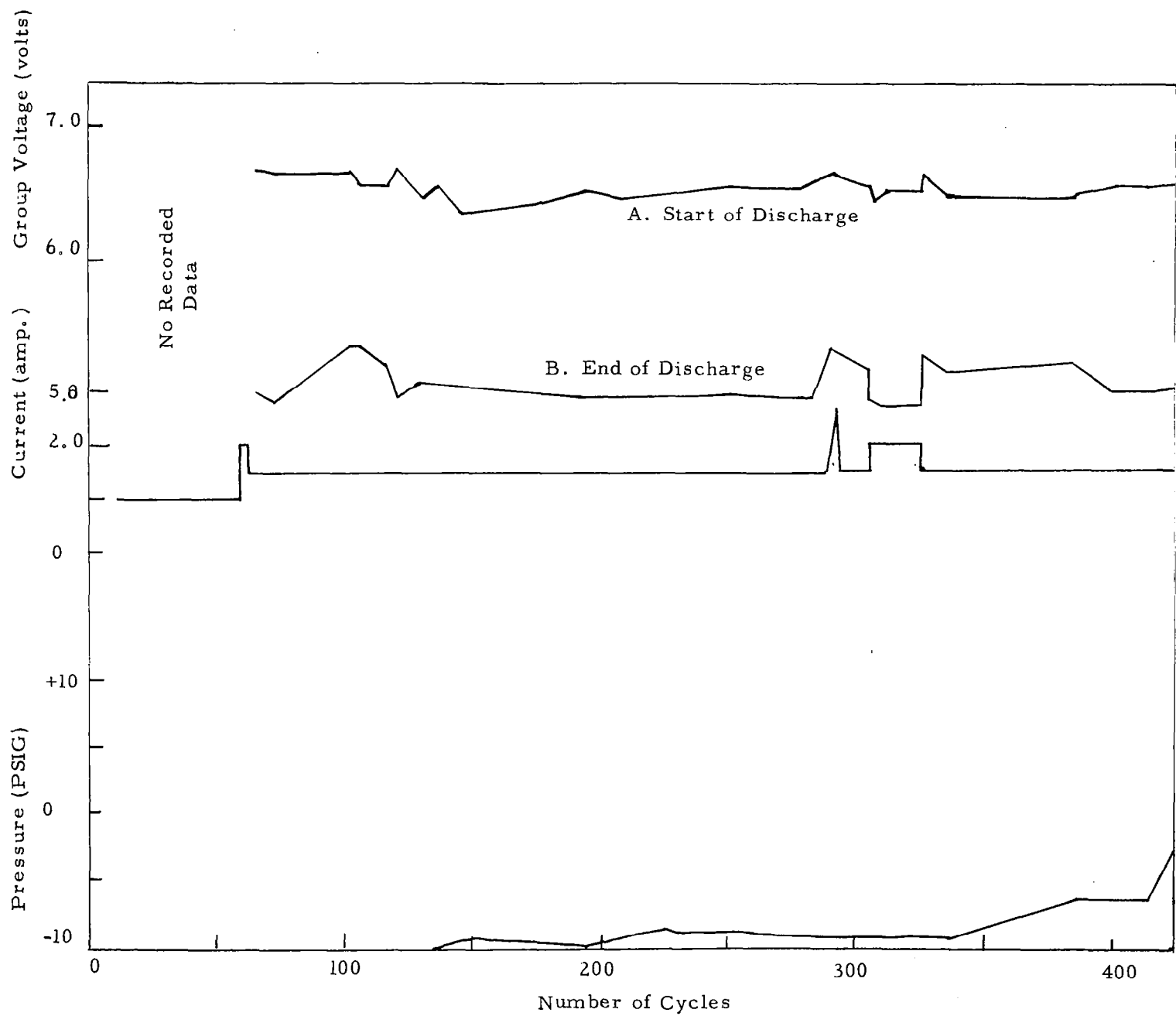


FIGURE 27 - Plot of Electrical Performance of Group N-X11 (5 cells) vs. Number of Cycles

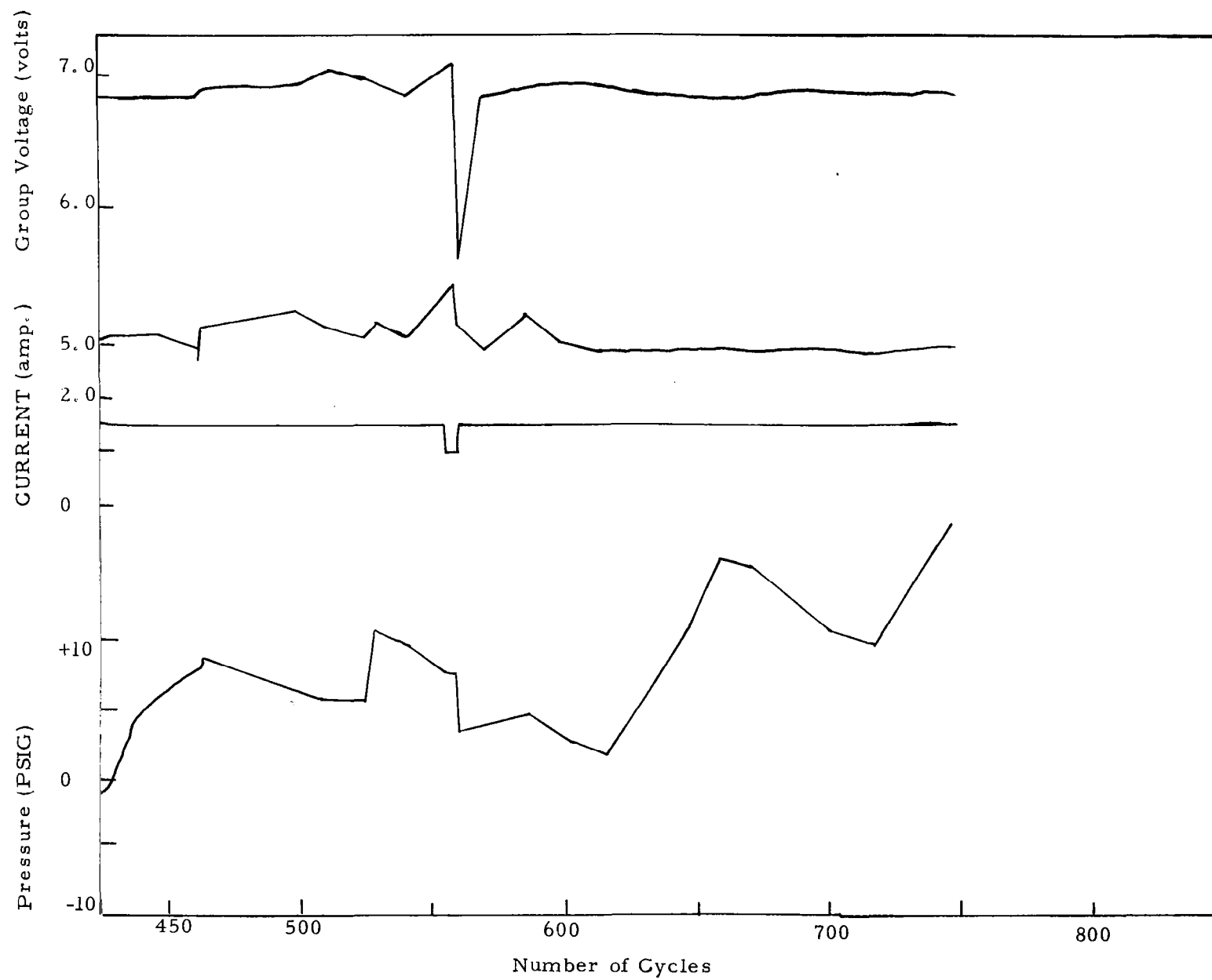


FIGURE 27 (Continued)

assumed from the behavior of overcharged cells on open circuit stand during the period of equipment repair. After an overcharge, the open circuit voltage declined from 1.40 volts, normal for the AgO electrode against cadmium, to 1.15 volts, normal for the Ag₂O against cadmium while the pressure for the corresponding times decreased from +21 to +1 psi. Based on the reasonable assumption of the accumulation of hydrogen, the data indicates that hydrogen does react with the silver electrode in these cells.

For the main portion of the tests, the cells were discharged at 1.5 amperes for 35 minutes or an output of 52.5 ampere-minutes. This capacity represents a depth of discharge of 40 to 50% of initial capacities for the four groups and of about 20% for Groups N-IX and N-X and about 35% for Groups N-XI and N-XII, basing the latter percentages for depth of discharge on the theoretical capacities of the negative plate groups. These figures are indicative for design purposes since the depth of discharge is more useful when expressed in terms of the rated capacity of cells. It will be indicated by subsequent data that the capacity of negative plates made from the ultra-fine cadmium powder improves with continued cycling. Additional data on cells with electrodes having the same negatives as Group N-IX are presented in the section on separator studies. It may be noted that these groups of cells were cycled together so that the results are subject to the limitations imposed by the charge acceptance characteristics of the group with the lowest performance.

Cells from each group were disassembled after 750 cycles. Generally speaking, the condition of the cells was excellent except on two important counts which led to further testing of the indicated cell structure. In the first place, the condition of the positive plates of Groups N-IX and N-X was unsatisfactory. These plates were of the brush-pasted AgO type. After the repeated cycling, the thin silver foil grid (0.0015" in thickness) had been almost completely converted to silver oxide. The applied active material was in a powdered form and much of it was dispersed within the absorbent separator (EM 341 dynel) around the plate. On the other hand, the condition of the negative plates in these two groups was excellent. Complete structural integrity of the negative plates was evident and indicative of a cold sintering of the original cadmium powder particles.

In the second place, the condition of the negative plates of the cells of Groups N-XI and N-XII was unsatisfactory. The negative plates lacked the desired coherence of the active material, particularly when in the discharged state. On the other hand, the positive plates of these cells were in excellent condition and showed little or no evidence of grid deterioration.

The observations made during disassembly and the testing data led to the conclusion that a combination of the plate types represented by the sintered positive plates of Groups N-XI and N-XII and by the cadmium powder negative plates of Groups N-IX and N-X would result in a cell of high capacity and excellent structural integrity. In order to balance the compositions of the active materials on assembly, it was decided to form the sintered silver plates electrochemically, carrying the oxidation to the AgO stage, then washing and drying the plates. The details of the design and assembly were the same as for the groups discussed in this section and are summarized in Table XXV under the assigned Group number N-XIII.

After a short formation charge, the group was given a manual discharge followed by a manually controlled charge to 1.60 volts per cell. The cells were then placed on automatic cycle using the 35/55 minute discharge/charge regime as in the previous Groups N-IX-XII. The discharge current was varied between 2.0 and 5.0 amperes with a constant potential charge of 1.60 volts per cell. The increase in cell capacity over the first 150 cycles is shown in Figure 28. In review of this phenomenon, it may be an advantage or disadvantage, depending on the cell use, that formation proceeds and requires the indicated number of cycles. The negative cadmium plate made by the pasting procedure utilizing ultra-fine cadmium powder should be studied from the point of view of the effect of extenders.

Cycling was also conducted at temperatures ranging from -20°F (-29°C) to $+120^{\circ}\text{F}$ (50°C). The limiting current for a 35-minute discharge is shown as a function of temperature in Figure 29. This limiting current represents the maximum current on discharge that can be maintained on discharge for the full 35 minutes of discharge and permit the recharge in 55 minutes at a constant potential of 1.60 volts per cell with a maximum current of five amperes. It is to be noted that no insulation of the battery groups was provided during the testing and that measurements indicated that the cells were maintained at temperature during cycle.

TABLE XXV

CONSTRUCTION OF GROUPS N-IX THROUGH N-XIII

Group	number	N-IX	N-X	N-XI	N-XII	N-XIII
Element						
Positive plates	number	6	6	6	6	6
Negative plates	number	7	7	7	7	7
Plate area, per side	sq. in.	2.5	2.5	2.5	2.5	2.5
Total conducting area	sq. in.	30	30	30	30	30
Separator system	+ to -	(Following separator system applies to Groups N-IX through N-XIII)				
	layer	1 - EM 341 dynel				
	layer	6 - 300 PUD-O cellophane				
	layer	1 - EM 341 dynel				
Electrolyte, KOH concn.	5 by wt.	40	40	40	40	40
Volume	ml.	16-17	16-17	16-17	16-17	16-17
Positive plates						
Type		Pasted AgO-----		Sintered Ag-----		Sintered and formed
Grid		Etched foil		Exmet 2/0		-
Thickness	mils	20	20	20	20	20
Active material						
AgO	g/plate	1.88	1.88	-	-	3.80
Ag	g/plate	-	-	3.90	3.90	-
Theoretical capacity						
amp-min/plate		49	49	116	116	99
amp-min/cell		294	294	696	696	594

TABLE XXV (Continued)

Group	number	N-IX	N-X	N-XI	N-XII	N-XIII
Negative plates						
Preliminary prototype	number	N-III	N-IV	N-VI	N-VIII	N-IV
Grid, expanded Exmet	Ag	5/0	5/0	5/0	5/0	6/0
Thickness	mil	20	20	20	20	20
Active material composition						
Cd	% by wt.	95	85	25	25	85
Cd(OH) ₂	% by wt.	0	10	75	70	10
Ag ₂ O	% by wt.	5	5	0	5	5
Active material weight						
Total	g/plate	1.93	1.91	1.46	1.21	1.80
Cd content	g/plate	1.83	1.76	1.20	0.95	1.67
Theoretical capacity						
amp-min/plate		52	50	34	27	48
amp-min /cell		312	300	204	162	288
Test capacity						
Initial average	amp-min	114	132	114	108	

FIGURE 28 Plot of Limiting Capacity vs.
Number of Cycles for Group N-X111

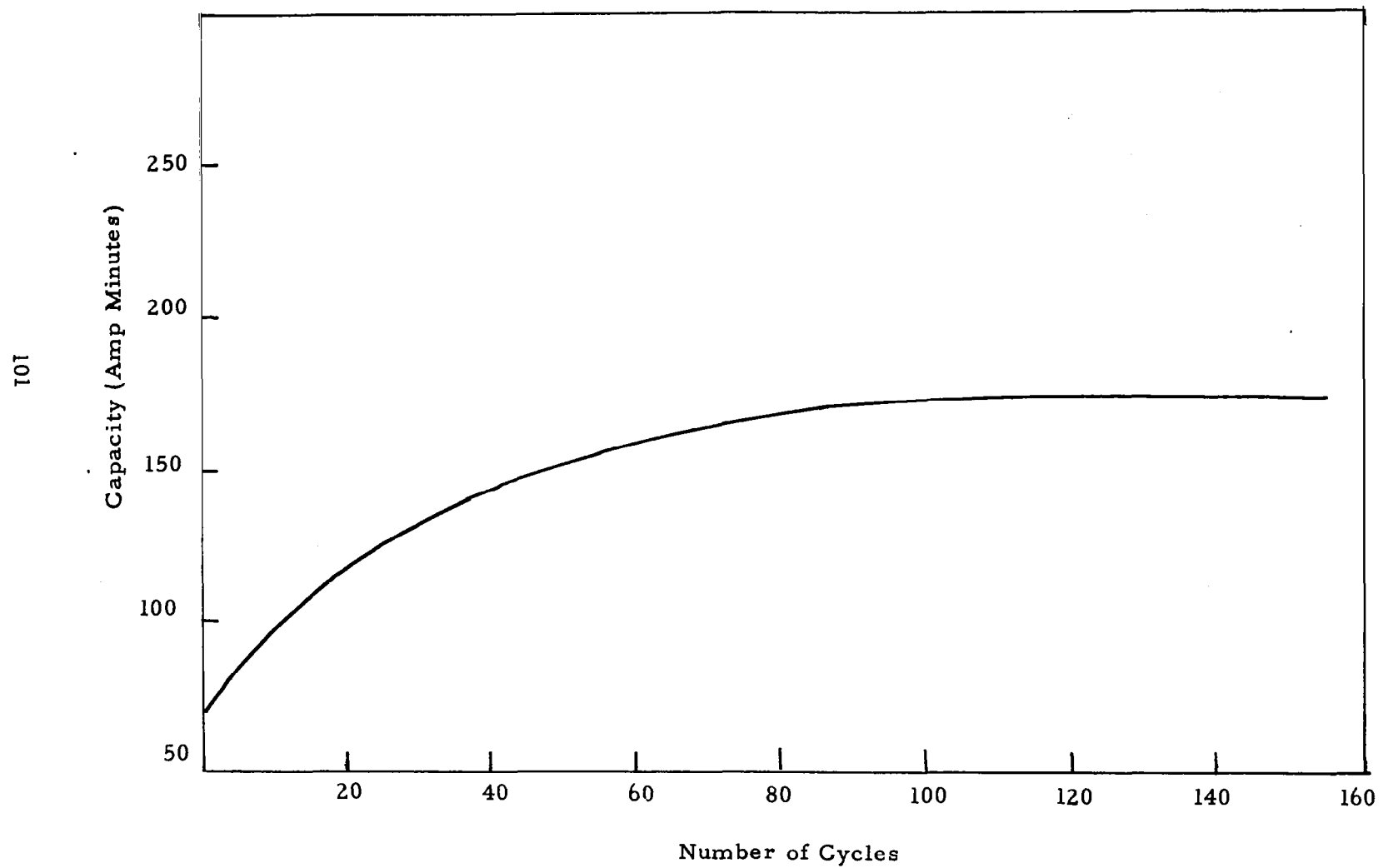
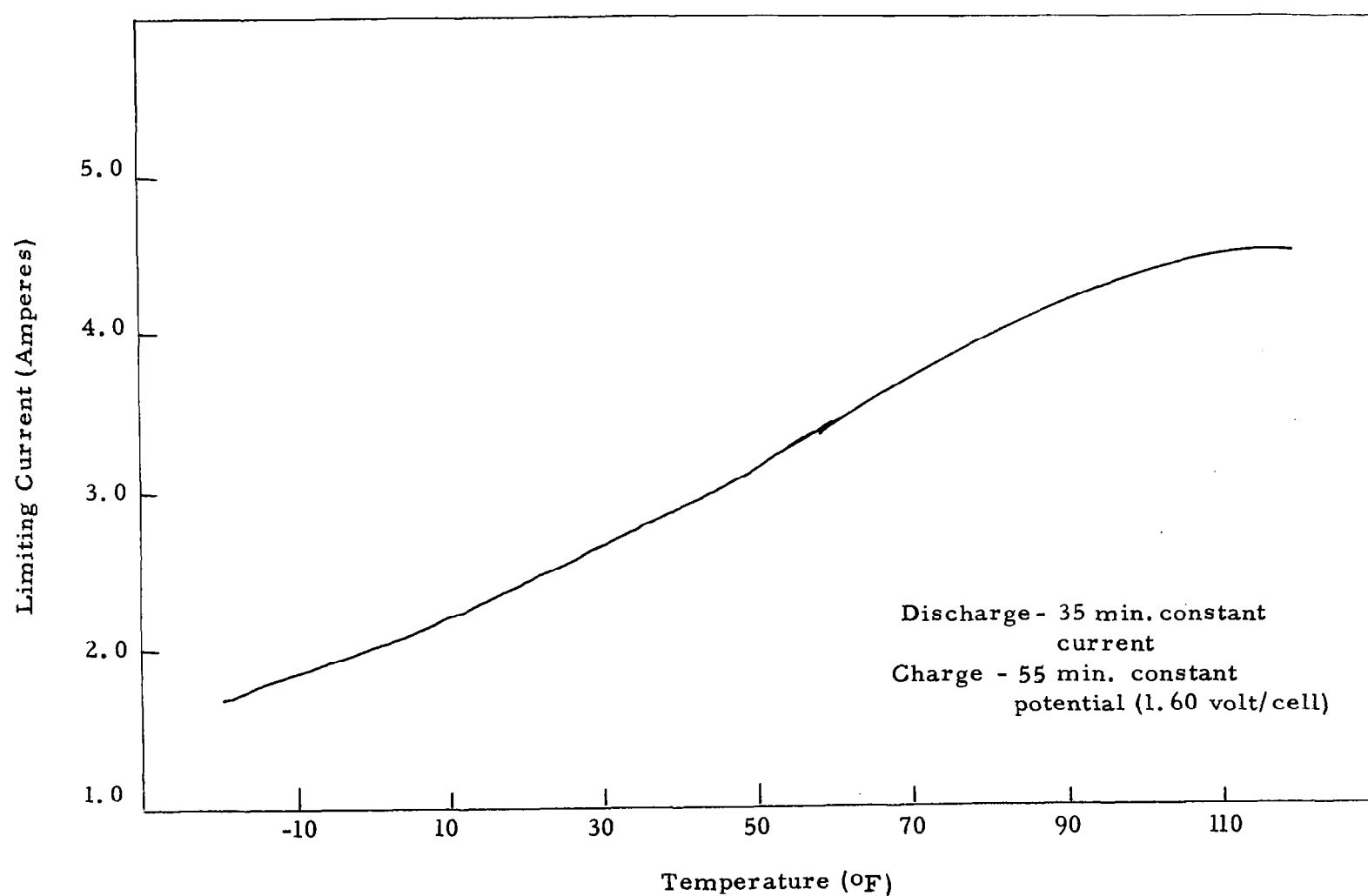


FIGURE 29 Plot of Limiting Discharge Current
vs. Temperature (Group N-X111)



C. Separator Studies

Initial screening of the possible membrane separators was done by means of review of available separator materials with regard to their known or reported properties. The particular properties which were considered were: (1) stability in strong potassium hydroxide solution; (2) stability to the strong oxidizing conditions prevalent at the positive electrode; (3) the electrical resistivity; and (4) the ability to retard penetration by silver particles. Two systems which had been under prior investigation were selected for use. These were the regenerated cellulose (Du Pont 300 PUD-O cellophane) and the combination of Polypor WA (Niemand Brothers) and the cellophane. Since the cellophane had been used as a standard separator for cells constructed under Section B, this system was chosen as a control for the evaluation of the other separator systems. The term separator system applies to the multi-layered assembly of separator materials which in this work will include a porous absorbent layer around each electrode and the barrier layers between the enveloped electrodes.

Our investigations and screening indicated that it was desirable to add two separators to this program. These two separators were Permion 300 and Permion 600 manufactured by Radiation Applications, Inc. The two separators are reported to be polyethylene and cellophane, respectively, with graft coatings of base exchange polymers. Table XXVI lists the properties as supplied by the manufacturer.

To evaluate the relative performance of the separator systems, four groups of five cells each were constructed. The construction of these cells was identified as Group N-IX (see Table XXV) with the exception of the membrane separator system employed and that all cells were equipped with normal vent plugs. In all cells, the plates (both positive and negative) were heat sealed in a non-woven dynel fabric (EM 341, Kendall Mills). The membrane separator system used in each of the groups is given as follows with order of separation listed from positive to negative:

Group S-I	Group S-II	Group S-III	Group S-IV (control)
2 layers Permion 300	4 layers Permion 600	2 layers Polypor WA	6 layers Cellophane 300 PUD-O
4 layers Cellophane 300 PUD-O		4 layers Cellophane 300 PUD-O	

TABLE XXVI

PROPERTIES OF PERMION 300
AND PERMION 600 MEMBRANES

	<u>PERMION 300</u>	<u>PERMION 600</u>
<u>Thickness</u>	1.5 mil	1 mil
<u>Electrical Resistivity*</u>		
30% KOH	10-30 milliohms/in ²	20-30 milliohms/in ²
45% KQH	40-50 milliohms/in ²	40-60 milliohms/in ²
<u>Membrane Potential</u>		
0.01 N/0.1 N K Cl	40-50 millivolts	none
<u>Stability**</u>		
In 40% KOH 165°F 200 psi	Completely Stable	250-1600 hours

* -- Resistivity of 1 mil cellophane - 30% KOH - 10 milliohms/in²
45% KOH - 10-15 milliohms/in²

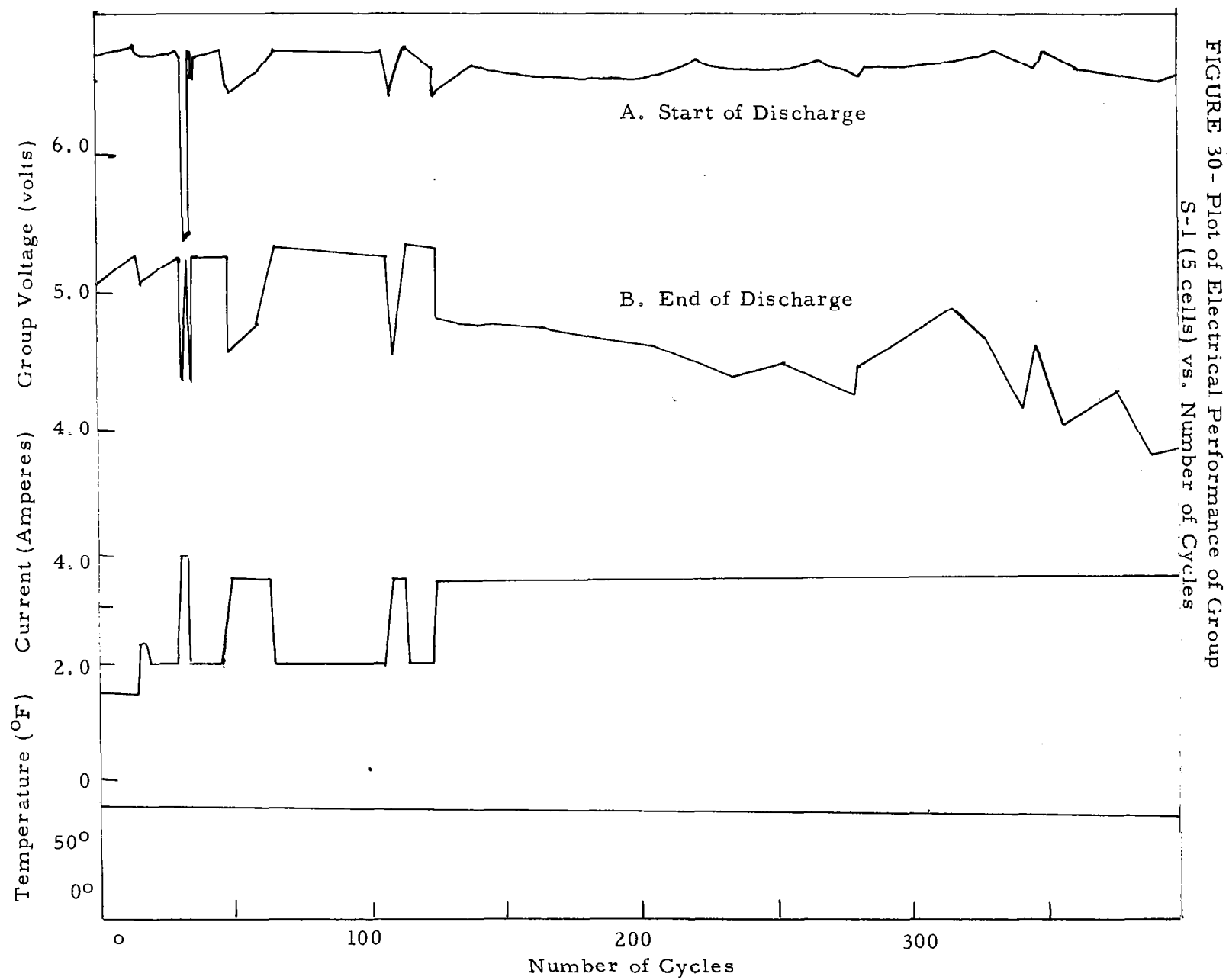
** -- Stability of 1 mil cellophane - 20 hours

NOTE: Data supplied by manufacturer, Radiation Applications, Incorporated,
36 - 40 37th Street, L. I. C. 1, New York

After an initial short charge, the groups were placed on an automatic cycle which consisted of a 35-minute discharge at various constant current rates and a 55-minute charge with a constant potential charge of 1.60 volts per cell with charge current limited initially to five amperes per cell group. The electrical performance of these groups is summarized in Figures 30, 31, 32 and 33. It is to be noted that the discharge currents for these cells are much higher and the effective depth of discharge much greater than was obtained for the comparable group (N-IX) in the negative plate series. After approximately 650 cycles, malfunction of the charge power supply resulted in continuous application of a constant current discharge current of 3.6 amperes during the discharge period without benefit of any recharge. This condition existed for at least eight cycle periods, and caused all cells to reverse polarity with accompanying gas evolution through electrolysis of the electrolyte. Internal pressure due to head and swelling of plates and separator caused the cell case to crack open on two cells.

The cells were recharged at a constant current of 0.10 ampere, during which time distilled water was added to the cells to replace that which had been lost due to the overdischarge. The cells were then discharged at 1.0 ampere to determine remaining capacity at this time. The cells were discharged to a cut-off voltage of 0.80 volts or to a discharge time of 210 minutes. (3.5 amp-hours). Discharge curves for one cell of each group as well as capacities of the other cells of the same group are shown in Figures 34, 35, 36 and 37. Since the lowest capacity obtained was in excess of 3.0 ampere-hours, this indicates that the relative efficiency of the cells and electrodes was very high even after the extreme conditions applied. Prior to the malfunction, all cells were cycling at 3.6 amperes which represents 43% of average theoretical capacity. The average actual capacity obtained for this discharge was 70.5% of the average theoretical capacity of the cells.

After recharge, the cells were replaced on automatic cycle and subjected to cycling under varying temperature and discharge load conditions. It was established that low temperature discharge performance was limited by the ability of the cells to accept charge during the time period.



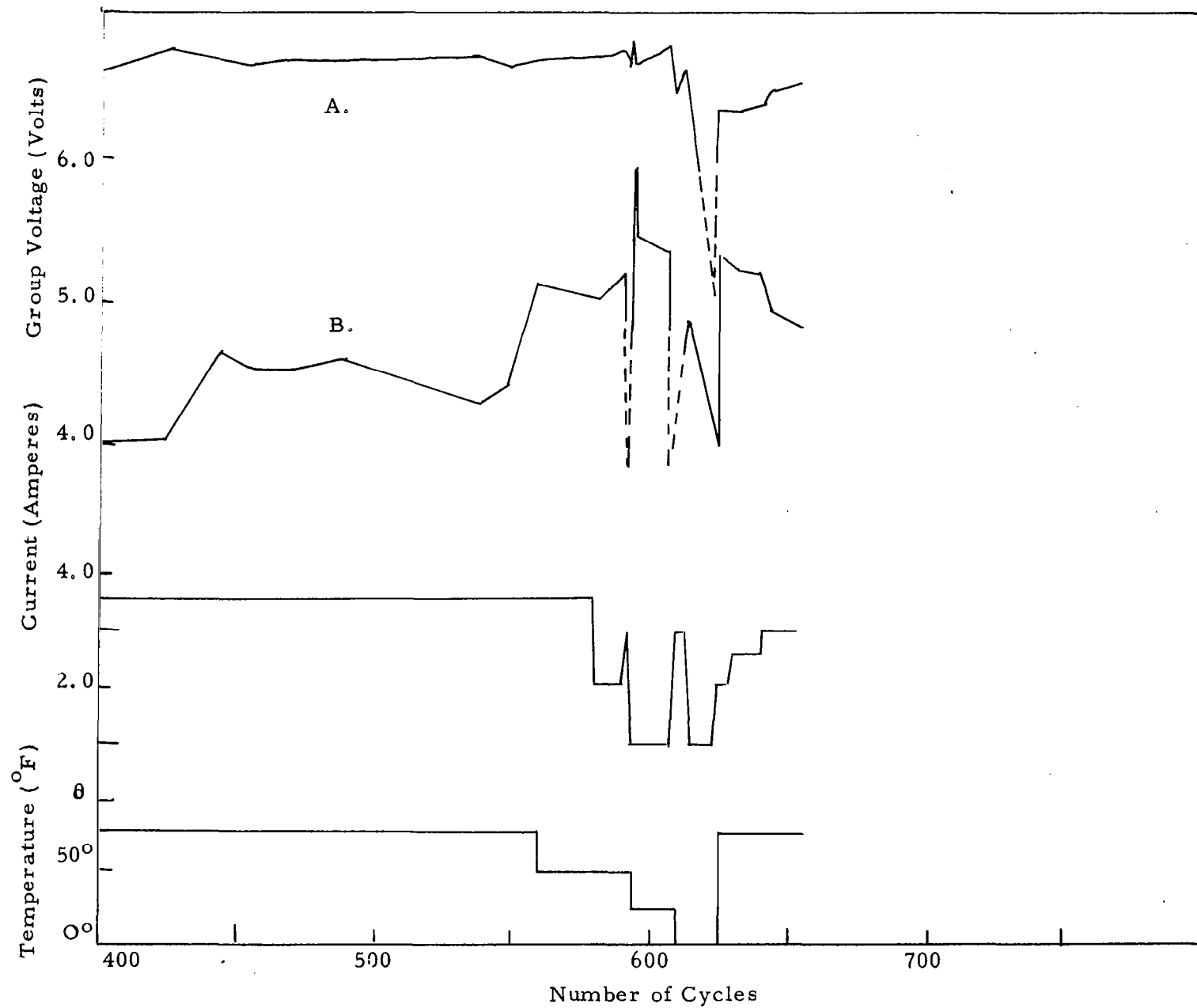


FIGURE 30 - (Continued)

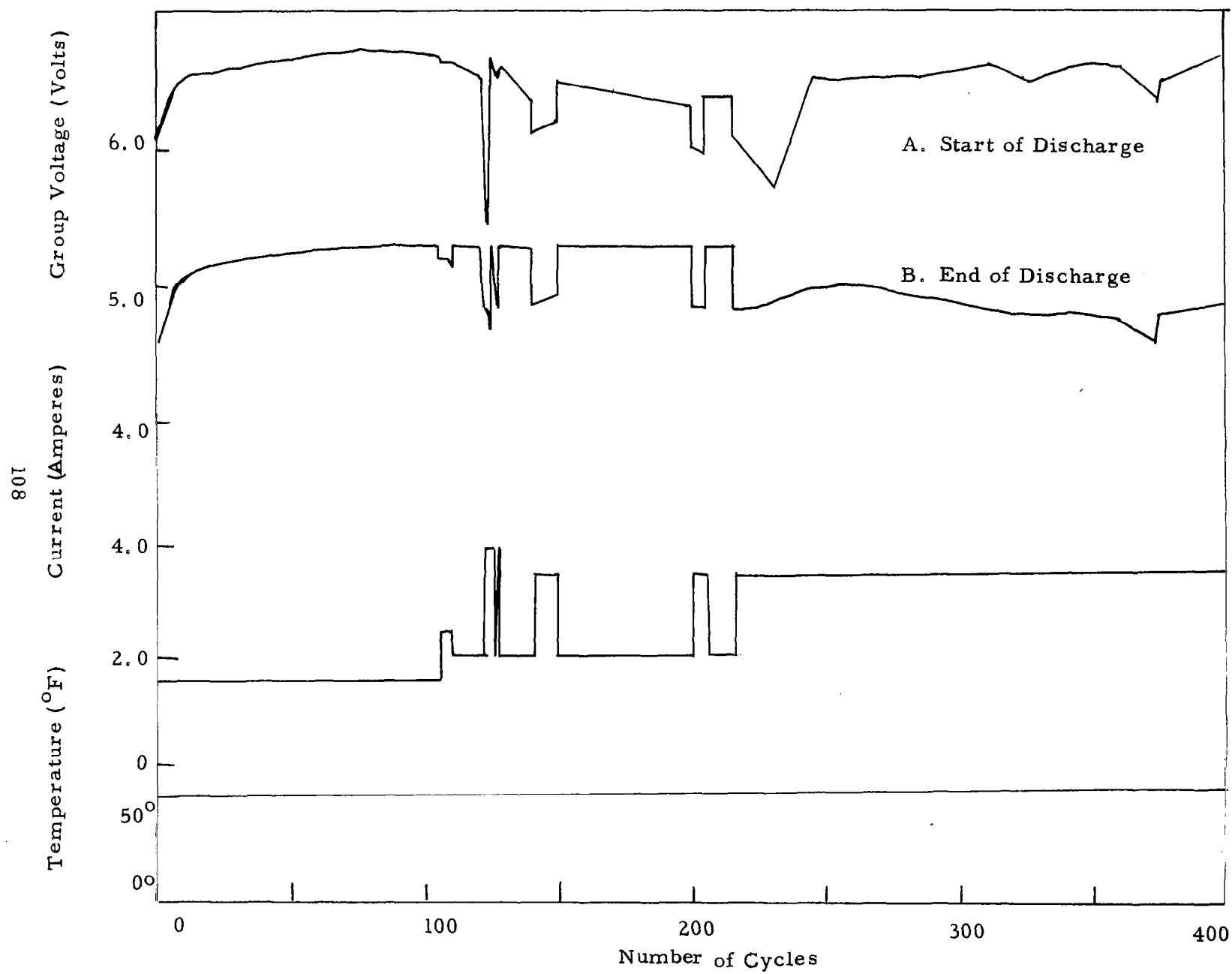


FIGURE 31- Plot of Electrical Performance of Group S-2 (5 cells) vs. Number of Cycles

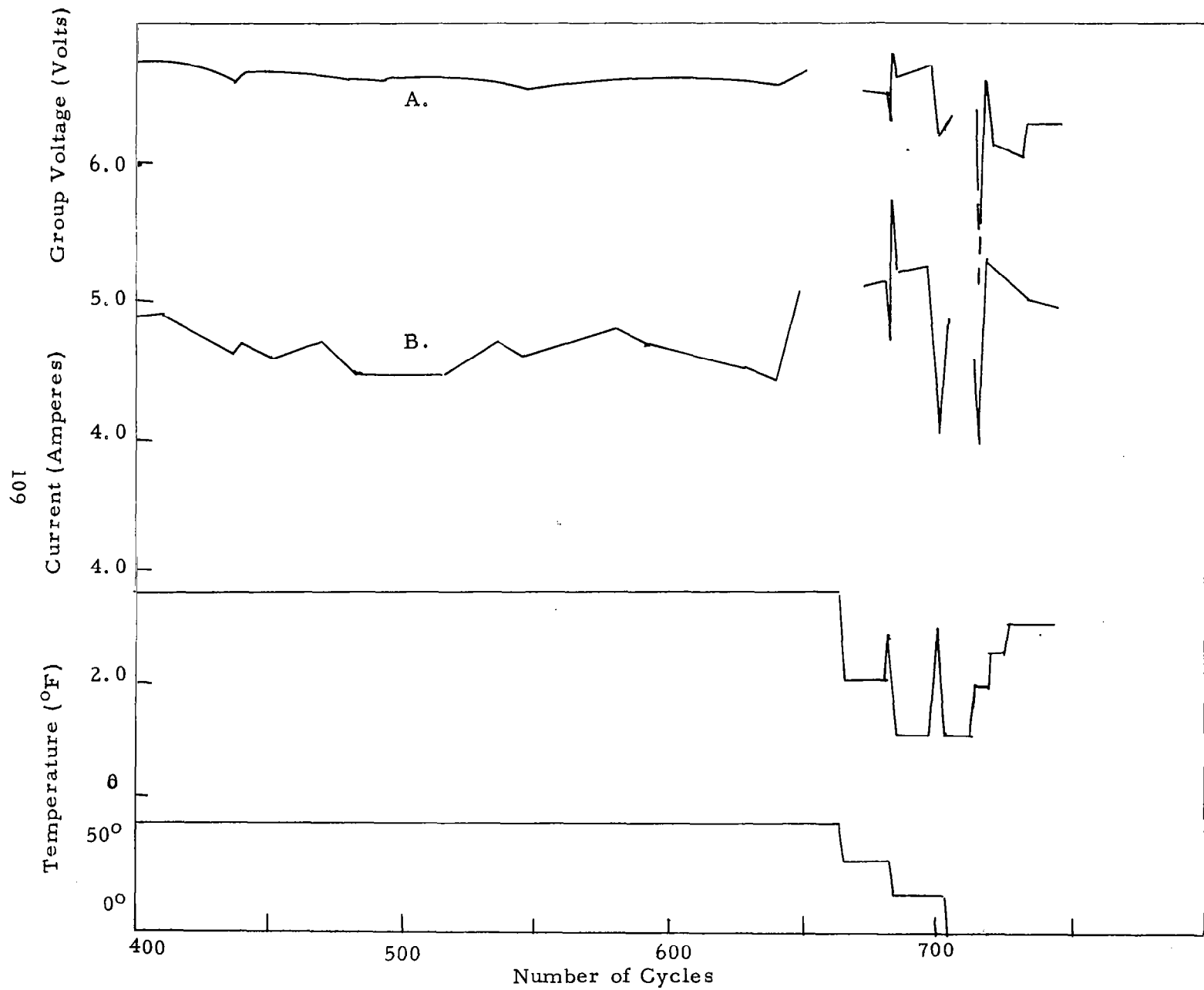
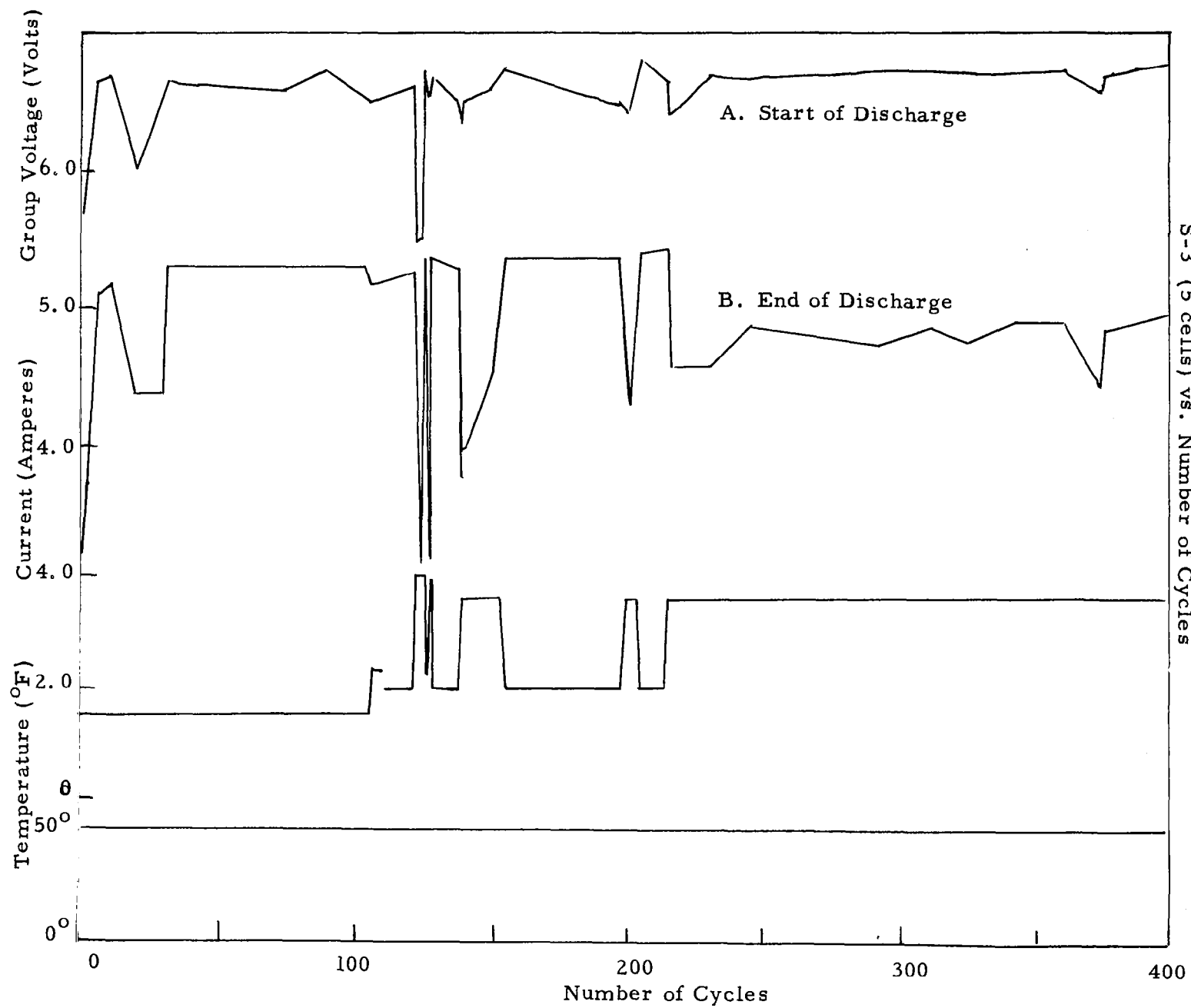


FIGURE 31 (Continued)



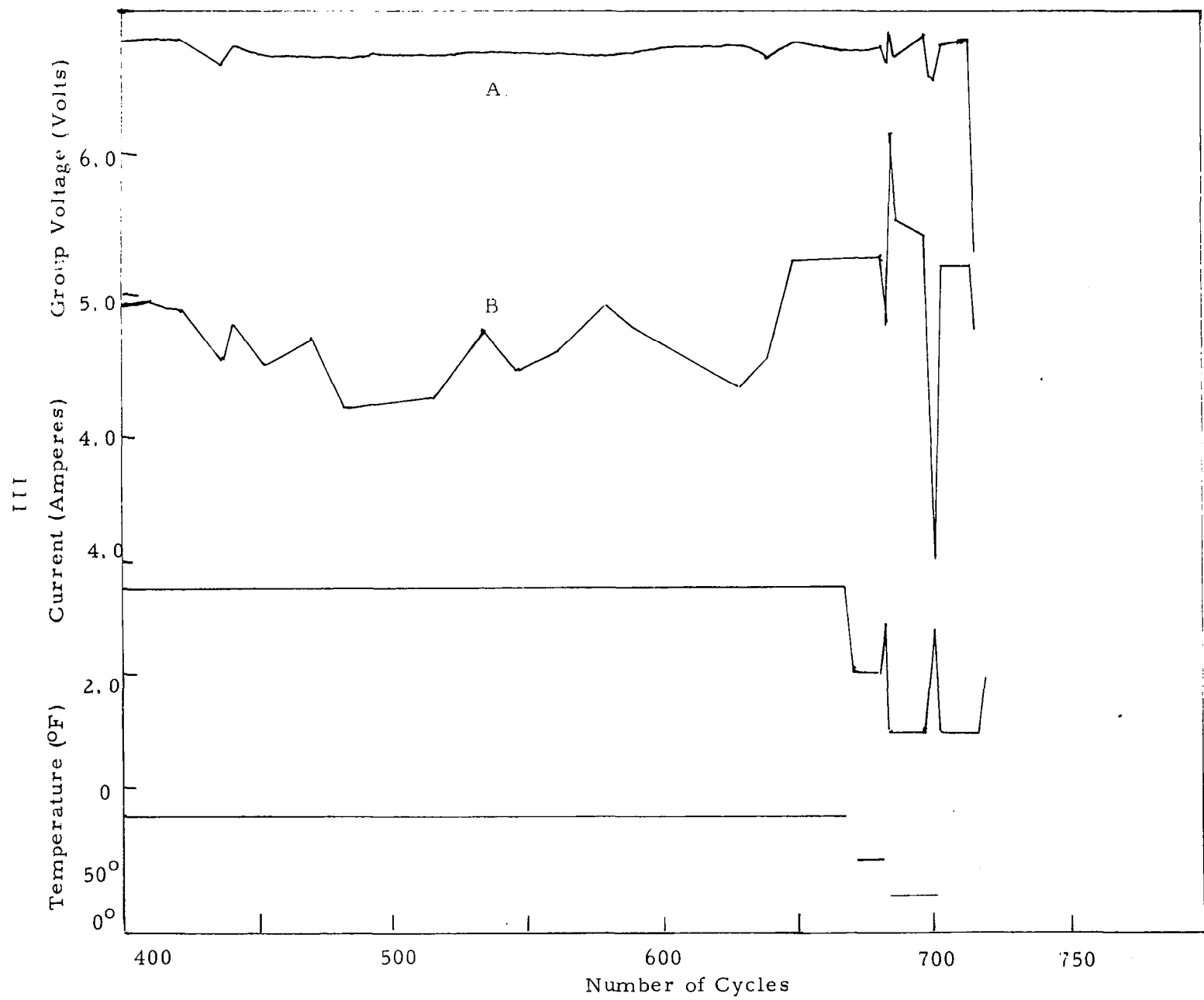


FIGURE 32 (Continued)

FIGURE 33 - Plot of Electrical Performance of Group
S-4 (5 cells) vs. Number of Cycles

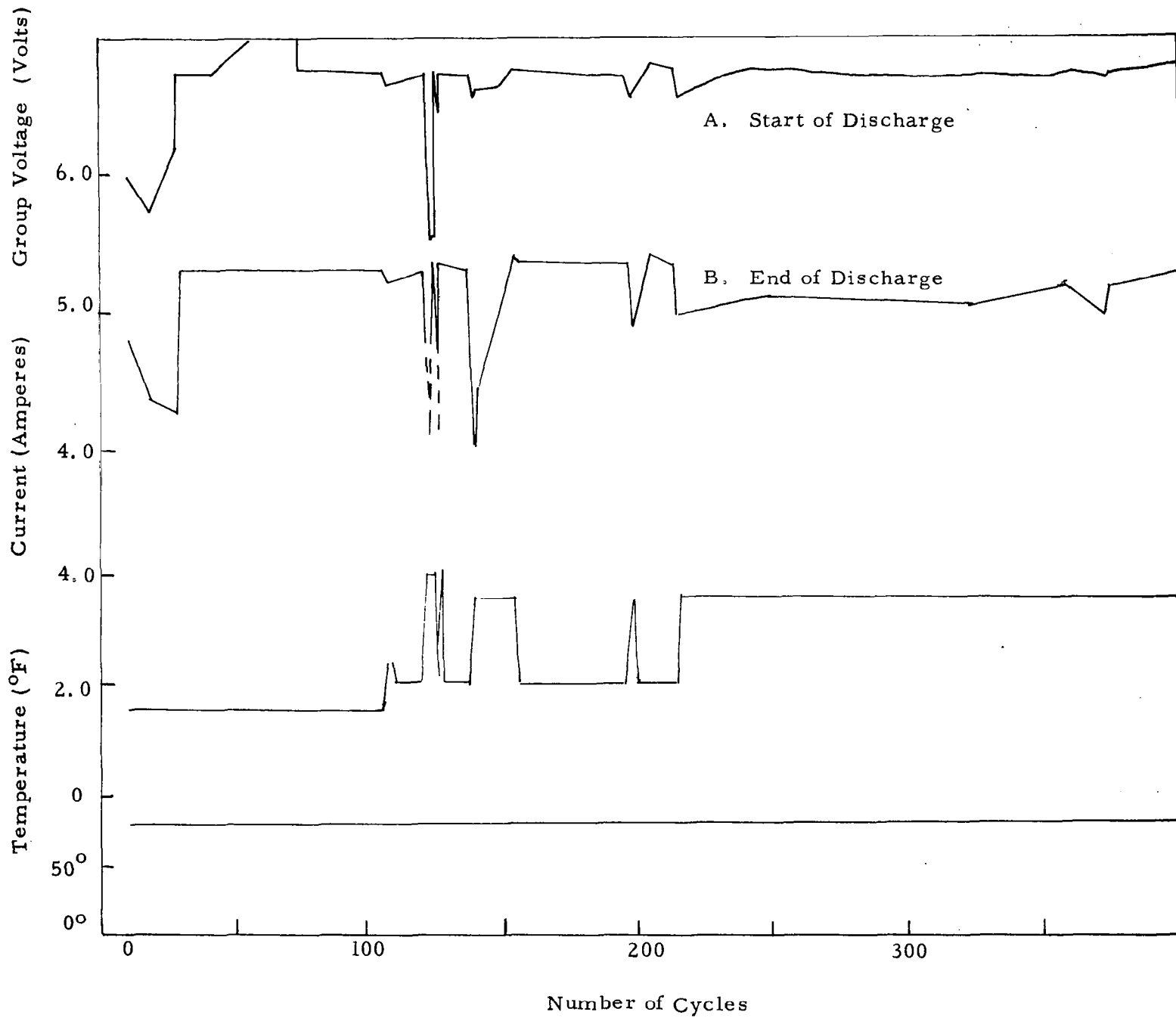


FIGURE 33 (Continued)

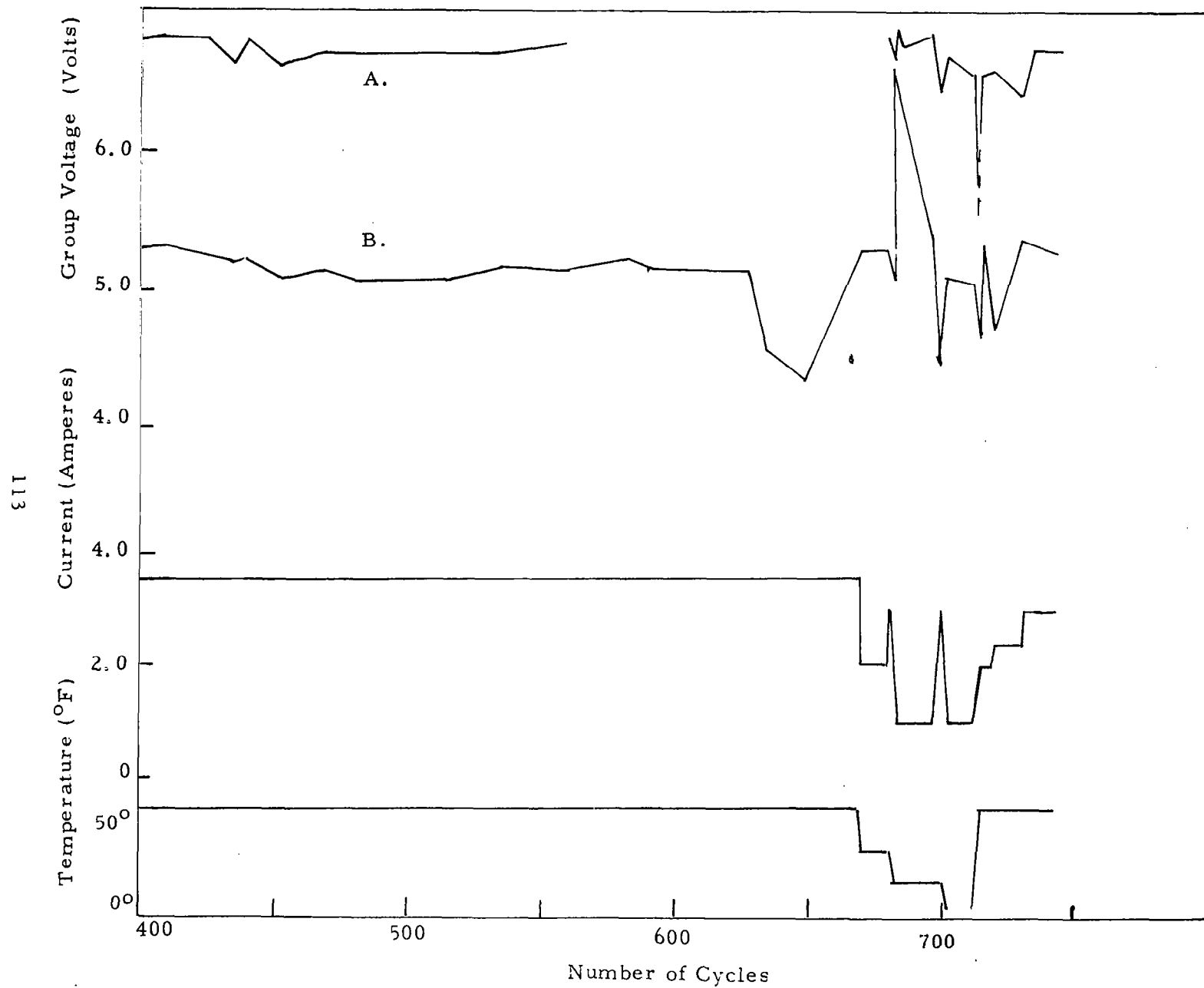


FIGURE 34
Voltage Curve Cell 5, Group SI
at 1.0 Amp Discharge

Cycle #574

Other Cell Capacities:
Cell #2- 210 + minutes
Cell #3- 210 + minutes
Cell #4- 190 minutes

114
Cell Potential (volts)

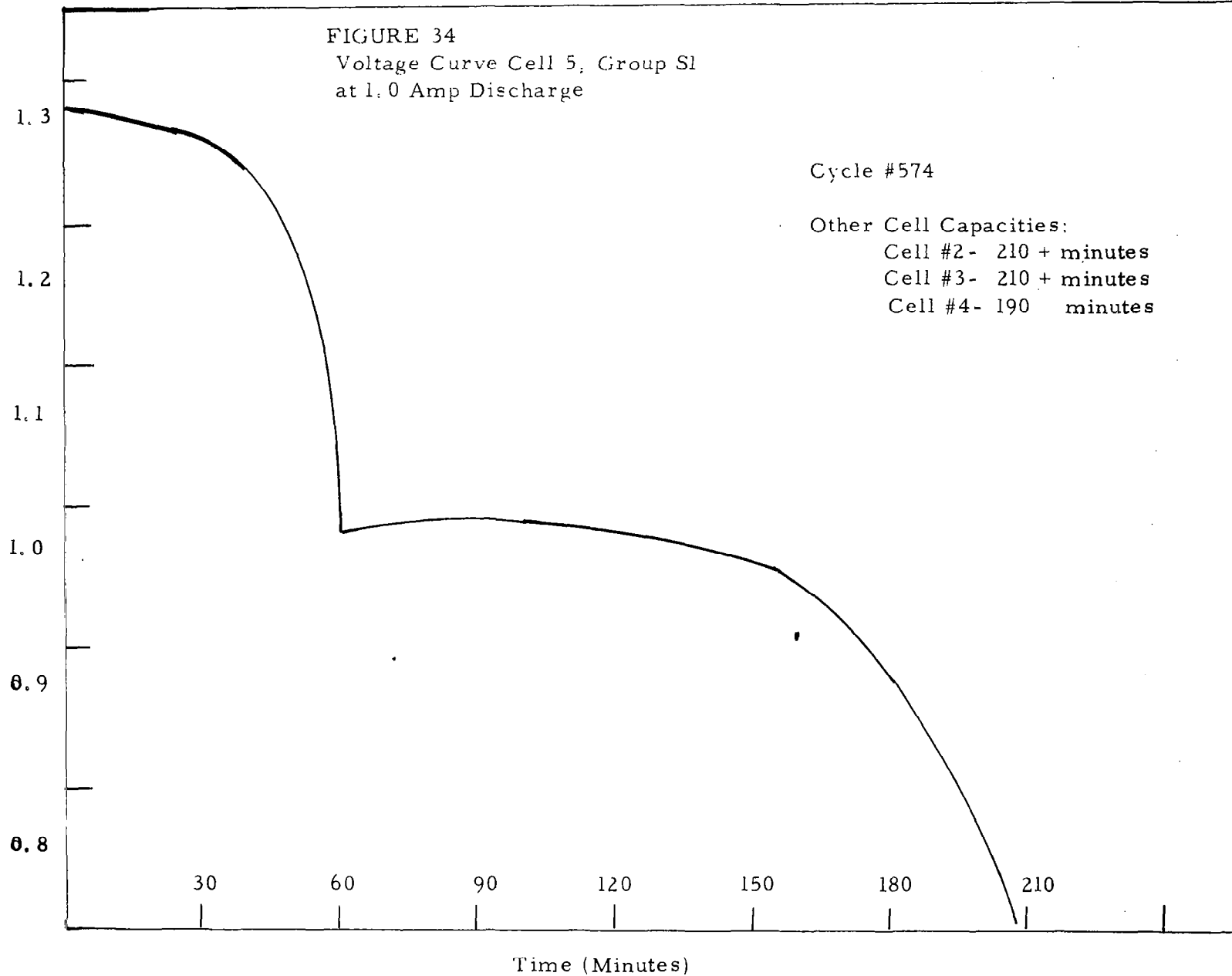


FIGURE 35- Voltage Curve Cell 1, Group S-2
at 1.0 Amp Discharge

Cycle No. 664
Other Cell Capacities

Cell No. 2 - 210 min.
No. 3 - 207 min.
No. 4 - 210 min.
No. 5 - 196 min.

511

Cell Potential (volts)

1.3
1.2
1.1
1.0
0.9
0.8

30

60

90

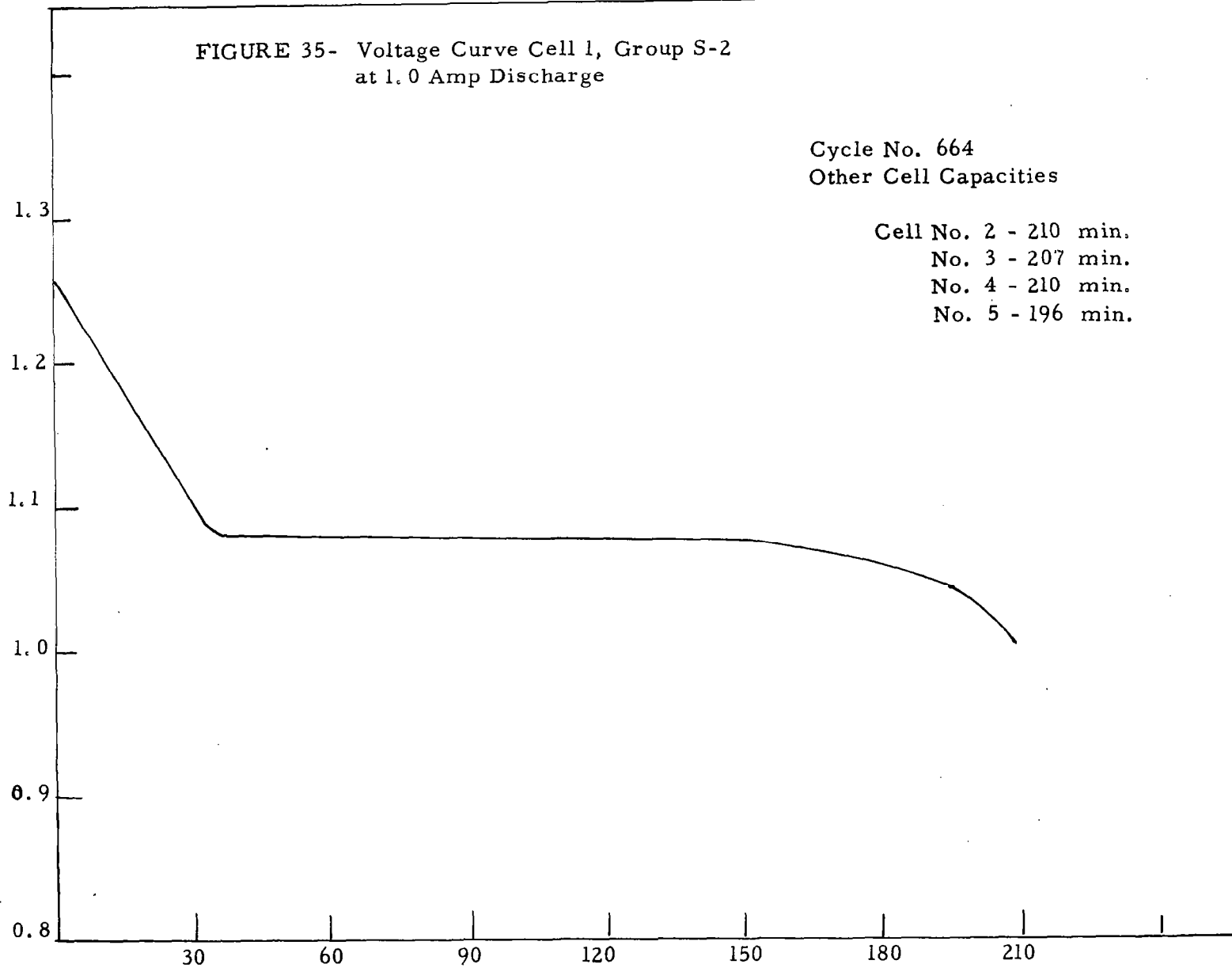
120

150

180

210

Time (Minutes)



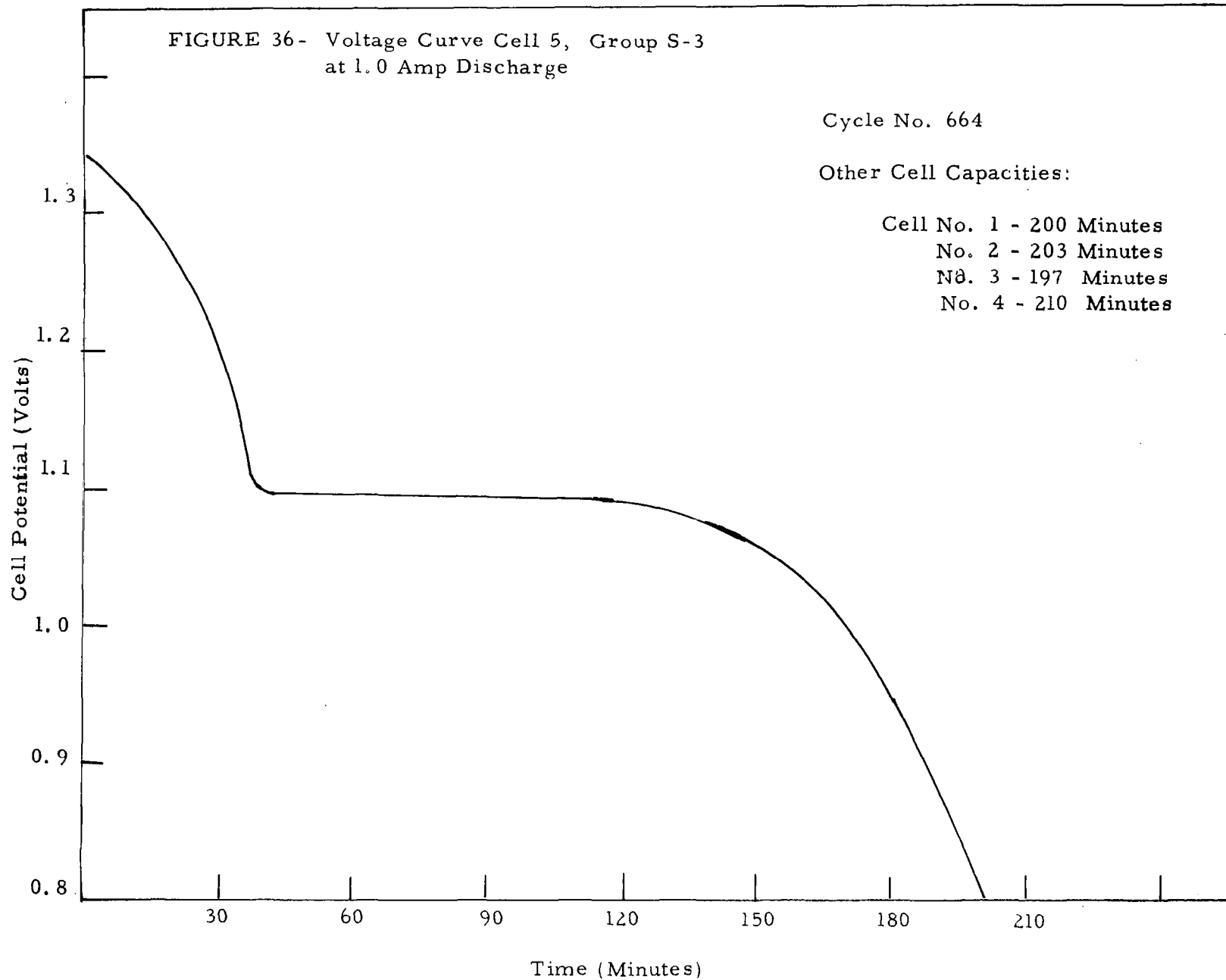


FIGURE 37 Voltage Curve, Cell 1, Group S-4
at 1.0 Amp Discharge

Cycle No. 653

Other Cell Capacities

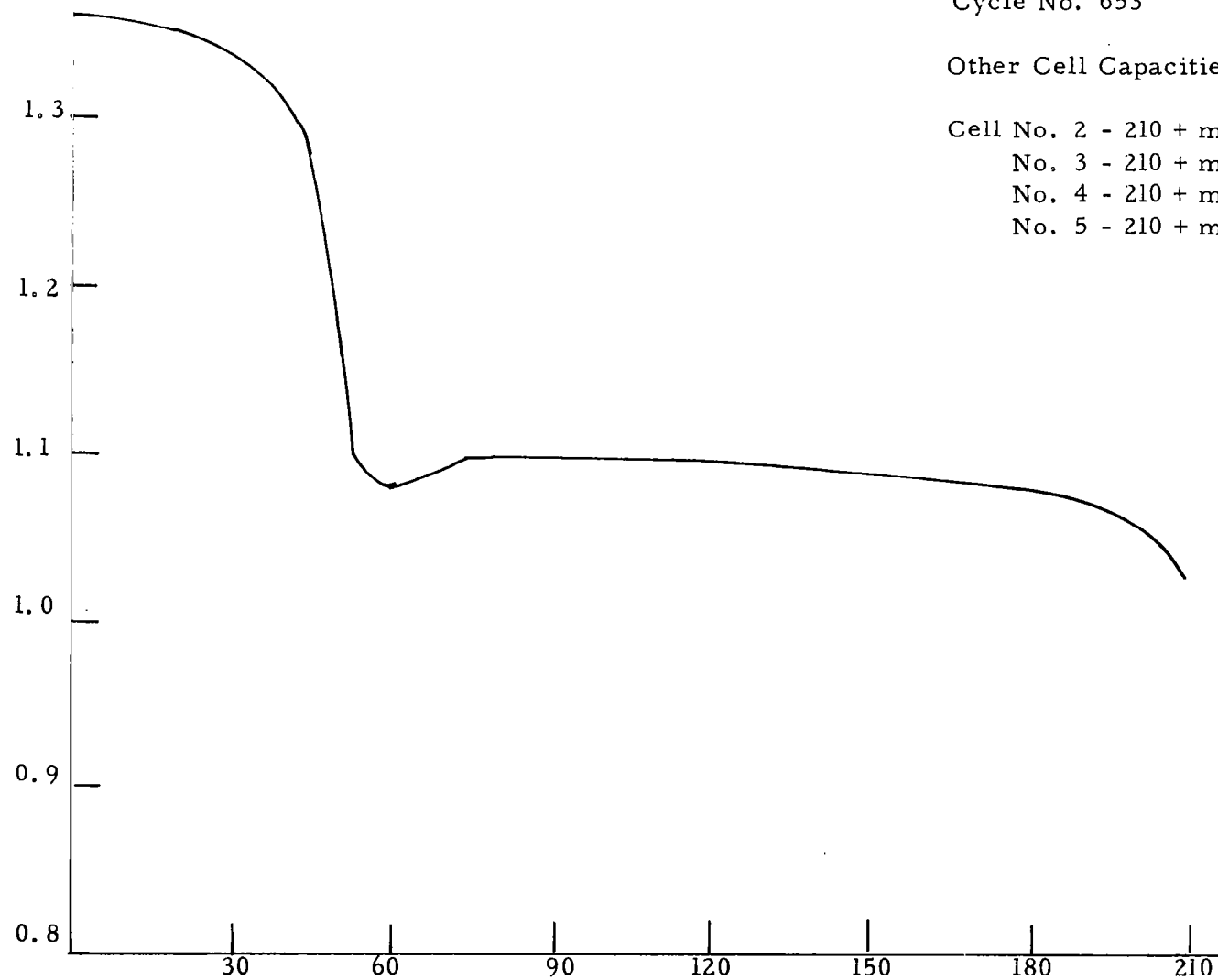
Cell No. 2 - 210 + min.

No. 3 - 210 + min.

No. 4 - 210 + min.

No. 5 - 210 + min.

117



Time (Minutes)

Representative cells were disassembled, the condition of the plates and separators was noted and silver content of the separators was obtained by analysis. The condition of the plates was the same as was noted for cells of this type in the preceding section. The positive plate material (originally pasted AgO on silver foil) was very loose and a portion of the material was impregnated within the structure of the non-woven absorbent first separator layer. The silver content in milligrams of silver per square inch is given for the various layers of membrane separator in the following table:

	GROUP			
	<u>S-1</u>	<u>S-2</u>	<u>S-3</u>	<u>S-4</u>
Separator System	2 layers Permion 300 4 layers Cellophane	4 layers Permion 600	2 layers Polypor WA 4 layers Cellophane	6 layers Cellophane
Number of Cycles	620	746	714	619
Layer (+ to -)	Silver Content (mg Ag/in ²)			
1	16	24.6	11.8	27.2
2	4.6	1.32	5.1	10.8
3	3.6	0.10	4.1	6.1
4	0.75	0.05	1.4	3.2
5	0.32	-	0.32	0.76
6	0.11	-	0.17	0.27

Though the silver content of the first layer is relatively high, there were indications that this was due to the filtering action of the membrane toward the loose particles of silver oxide. When a section of a first layer was washed and dried, conductivity was detected on the surface next to the positive plate (300 ohms over a 0.5 inch distance) but could not be detected on the opposite side or through the section of the 0.001 inch thick cellophane (resistance in excess of 1,000 megohms).

From the table it is clearly evident that the membrane separators which are not capable of reducing silver oxides to silver, or have some ion-exchange activity are more effective in decreasing the silver migration.

The most effective separator, in terms of lower silver content of the latter layers, was the Permion 600. It is to be further noted that this separator retained its original strength after over 700 cycles and had no tendency to develop cracks or tears. It is considered that the Permion 300 was more effective than the Polypor WA in terms of overall performance and in effectiveness per unit thickness. This separator would be recommended for use adjacent to the positive plate.

VII. PROTOTYPE EVALUATION

A. Fabrication of Cells

Based on the findings of Sections VI. A through C, seven additional prototype cells were built. The first two of these, cells G and H, were constructed using fabricated cell cases having internal dimensions comparable to those shown for the molded case shown in Figure 38. These cases were machined from acrylic tubing and sheet. The cells were fitted with conventional terminals to facilitate individual cell testing.

All cells consisted of eleven plates, five positives and six negatives, with each plate heat sealed in absorbent non-woven dynel separator. Details of cell constructions and test results are summarized in Table XXVII. The following features were common for all cells:

1. Positive Plate: Resin bonded silver powder was sintered to each side of expanded silver foil to make the active electrode material. The plates were cut to size, and silver wire was spot welded to the plate to serve as plate tabs. The plates were electrochemically anodized in 20% KOH solution to the divalent oxide state. The plate area was 4.0 square inches.
2. Negative Plate: The negative plates were prepared by applying an active material paste to an expanded silver foil grid. The active material consisted of 85% cadmium, 10% cadmium oxide, and 5% silver (I) oxide. Sufficient quantity of a 2% polyvinyl alcohol solution was added to produce a workable paste. The area of the negative plate was 4.0 square inches.
3. Electrolyte: A 40% solution of potassium hydroxide was used for the electrolyte. In all cases, a 72-hour minimum soak period was provided for cell equilibrium prior to cell testing.

Cell G was constructed using positive plates as described above, with a final plate thickness of 0.020 inch, and a silver density of 1.5 grams of silver per square inch. The separator, in addition to the plate wicks, was four layers of cellophane.

FIGURE 38
SEALED SILVER-CADMIUM CELL
P/N 201321

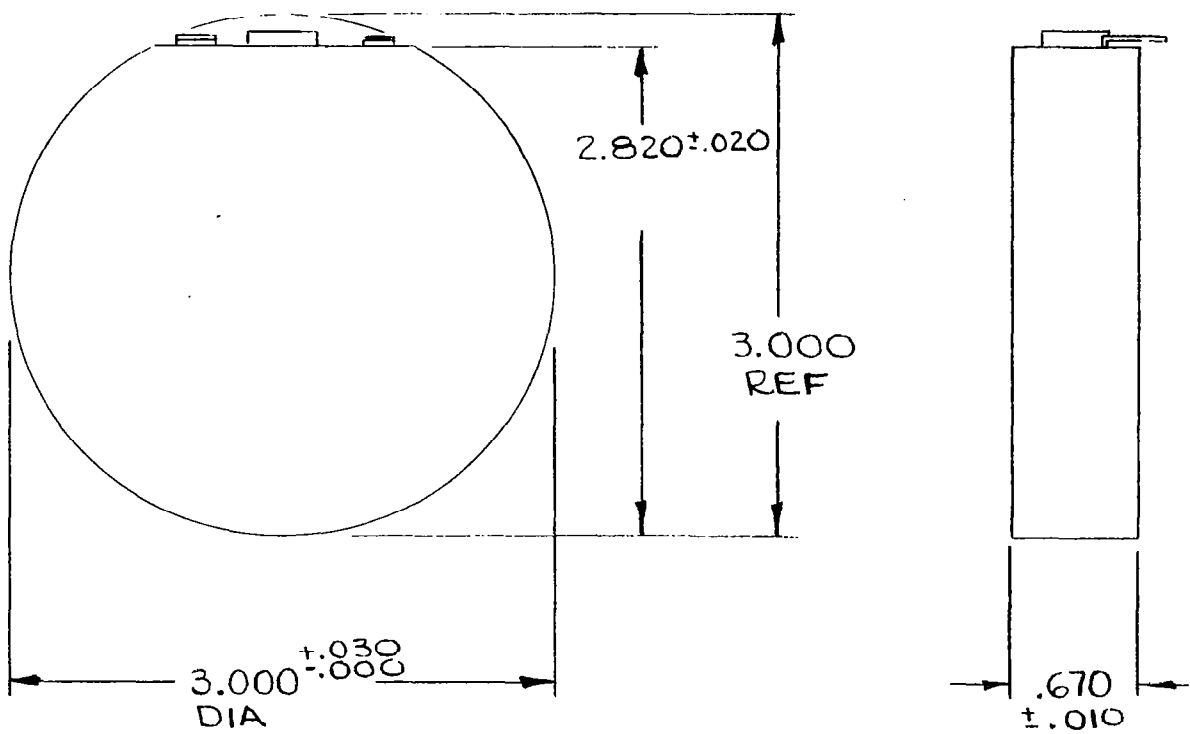


TABLE XXVII

PROTOTYPE TEST CELLS

<u>Cell</u>	<u>Positive Electrode</u>	<u>Negative Electrode</u>	<u>Separator</u>	<u>Test Results</u>
G and H	Formed AgO RB .020 Exmet 5 plates	Pasted 85 Cd 10 CdO 5 Ag ₂ O 2 PVA Exmet 6 plates	1 - EM 341 4 - PUD-O 1 - EM 341	Three cycles at 2 A C. C. discharge Two cycles at 4 A C. C. discharge Assumed CD = 0.05 and .10 Solvent seal ruptured
I and J	AgO formed Exmet 4 in ² 5 plates	85 Cd pasted 10 CdO 5 Ag ₂ O 2 PVA Exmet 4 in ² 6 plates	1 - EM 341 2 - Permion 300 2 - Permion 600 1 - EM 341 + spacer rings	Cell I - internal short Cell J - 214 cycles at CD = 0.025
K L M	AgO formed Exmet 4 in ² 5 plates	85 Cd pasted 10 CdO 5 Ag ₂ O 2 PVA Exmet 4 in ² 6 plates	1 - EM 341 1 - Permion 300 4 - Permion 600 1 - EM 341 + spacer rings	Cell K not tested Cell L - 265 cycles at 0.025 CD/3 cycles at 0.0375 CD Cell M - 148 cycles at 0.025 CD/50 cycles at 0.0375 CD

Cell H was a duplicate construction of cell G.

Cell I used the same plate constructions as cell G. The separator system, in addition to plate wicks, was two layers of polyethylene base ion exchange membrane (Permion 300), and two layers of modified cellophane (Permion 600) -- from positive to negative. Sealing of the membrane separators around the positive plates was accomplished by the use of spacer rings which provided a pressure seal against the swellable membrane layers.

Cell J was a duplicate construction of cell I.

Cells K, L and M were evaluated for the purpose of selecting a final prototype design. The various configurations are shown in Figure 39.

Cell K: In this configuration, the negative plate was first heat sealed in a dynel envelope, and then was subassembled into a package consisting of four layers each of modified cellophane cemented to each side of a compression ring. The positive plate was heat sealed in an envelope consisting of one inner wrap of dynel and one outer wrap of the polyethylene membrane. One positive envelope was then positioned between two negative subassemblies to the total configuration listed above. This was an extension of the configuration of cells I and J. The seal was made at the cemented ring-separator joint.

Cell L: Positive and negative plates for this cell were made up in envelopes as described above. However, each plate (positive and negative) was positioned inside a compression ring, making a total of eleven rings. Four layers of the modified separator were placed between each ring -- a total of ten four-layer packs. The seal system was ring/separator (four layers).

Cell M: Plates for cell M were made in envelopes as described for cell K. The distinction in this case was that instead of the alternate ring-separator system, described for cell L, the rings were doubled. In effect then, the seal was separator to separator at the positive plate, with the negative plate positioned between the double rings.

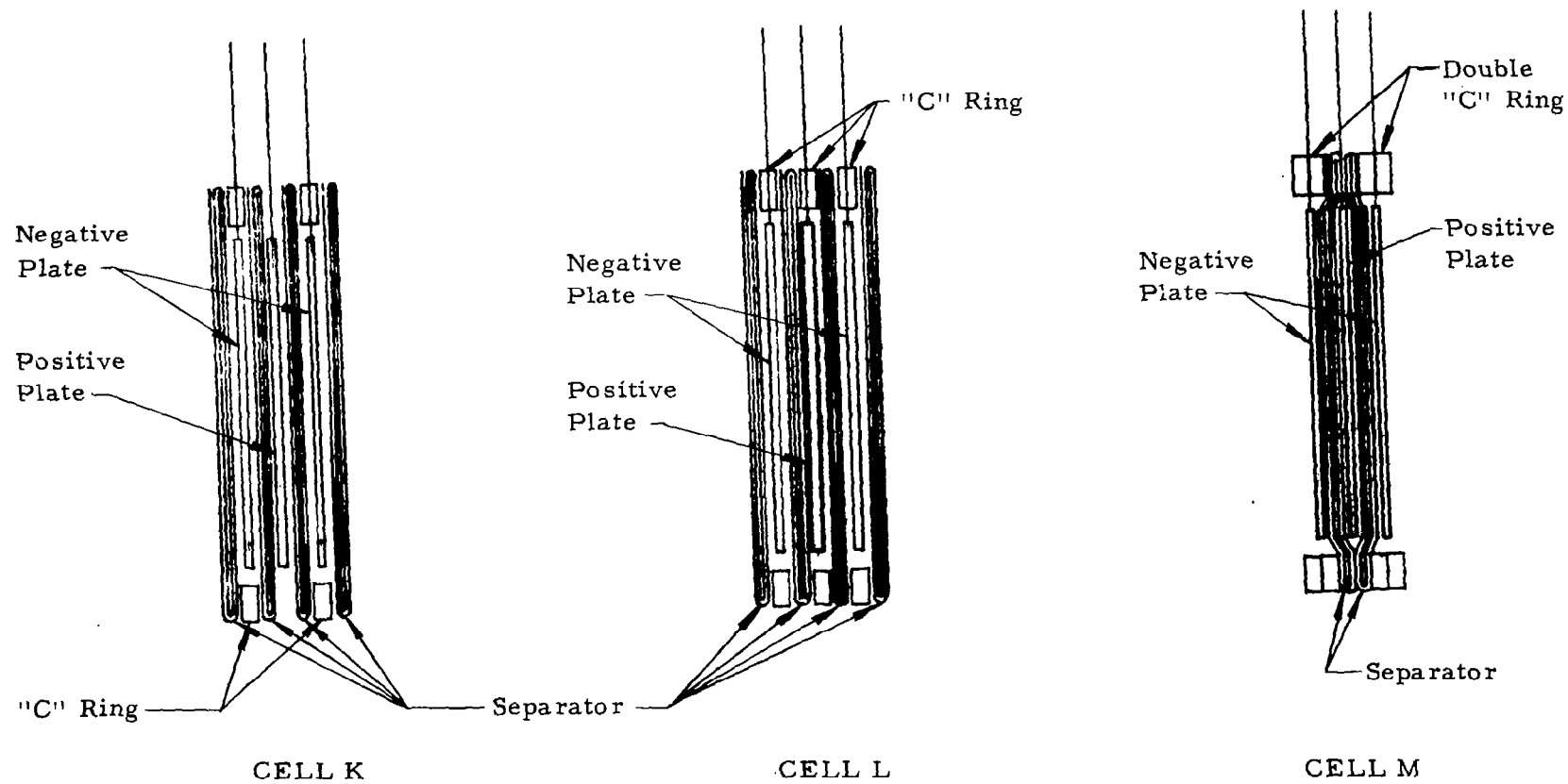


Figure 39 Various Cell Constructions

Cells P1 - P5: Five additional cells were built to the same configuration as cell M. This design was selected for the Phase III effort. The cells were cycled; the results are reported under Testing of Cells.

B. Test Results of Prototype Cell Constructions

Cells G and H: The performance of these cells over the first few cycles is shown in Figure 40. This graph shows a plot of voltage against capacity for representative cycles. As indicated by this plot, the capacity is increasing even with an increasing rate of discharge. This type of behavior is characteristic of the type of negative plate used. Previous tests on cells of this type indicate that the capacity would increase to approximately 500 to 600 ampere-minutes over the first 100 cycles. After five cycles, a cement joint in the fabricated cell cases developed a severe leak, thus precluding the possibility of further cycling on these cells. Since this type of joint was made with solvent cement, it was inherently weaker than that formed with a catalytic type cement. Succeeding cells were fabricated with catalyzed styrene cement.

Cell I: This cell indicated an internal short circuit when initially cycled. The short that developed was due to a lead wire which became bent during assembly. As this cell had been used to work out assembly details, and had been taken apart and re-assembled several times prior to its final seal, this was not considered to be significant for future construction.

Cell J: This cell was given initial manual cycle tests; its performance at this time was quite similar to cells G and H. It was then placed on automatic cycling, with a constant potential charge at 1.56 volts for 55 minutes, and a 1.0 ampere constant current discharge for 35 minutes. The charging current was limited to 1.0 ampere. This schedule was followed for 124 cycles, then was changed to combine two cycles, one cycle with a 120-minute charge and a 60-minute discharge, and 14 cycles of the 55/35-minute type. The cycle history of this cell is shown in Table XXVIII. Typical voltage and current curves for the two length cycles are shown in Figures 41 and 42.

FIGURE 40

Cell No. G

11 plates Room Temperature

Cycle #

Discharge Rate

1

2.0 amps.

3

2.0 amps.

4

4.0 amps.

5

4.0 amps.

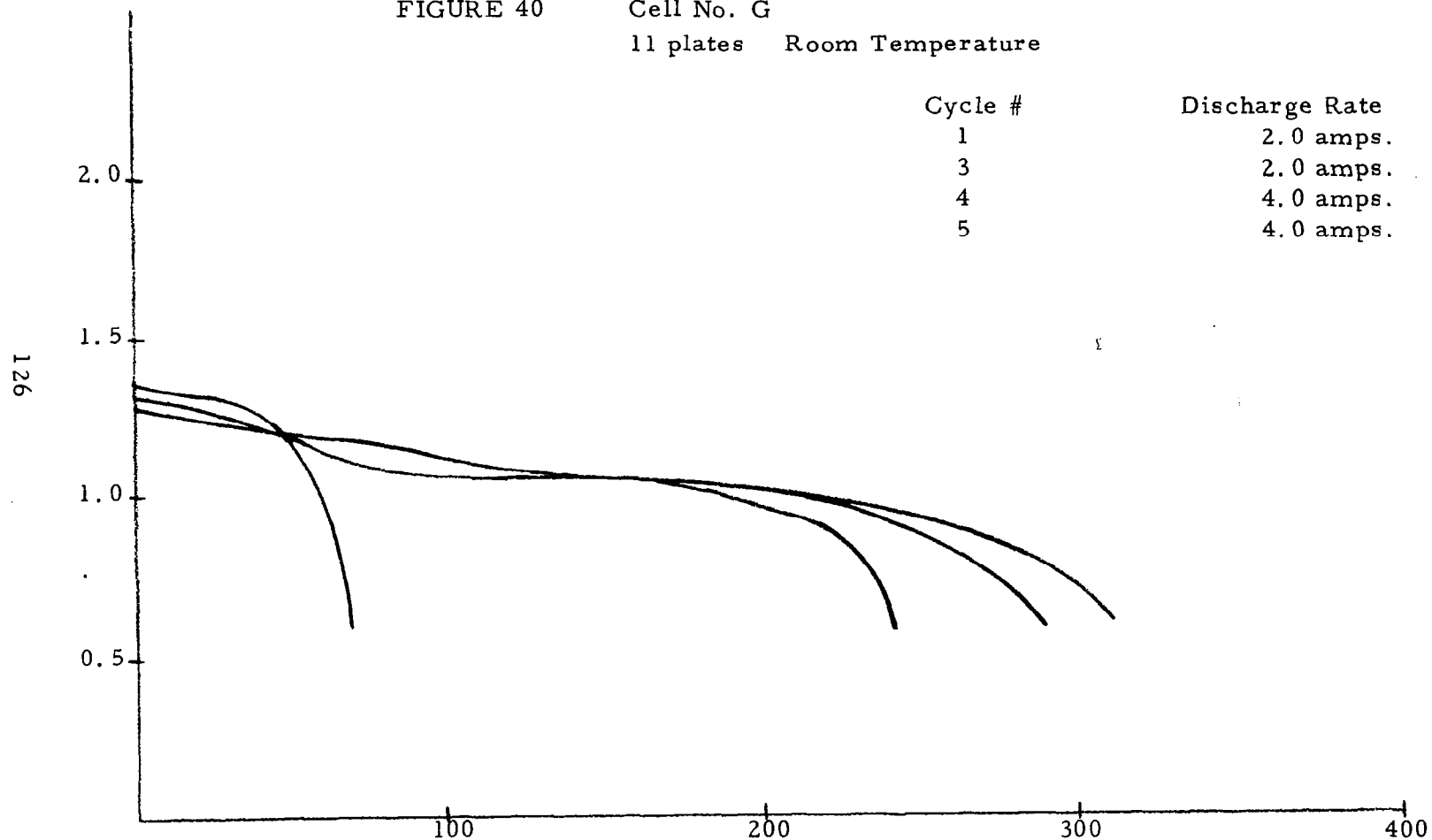


Figure 41 Cell J 90 Minute Cycle

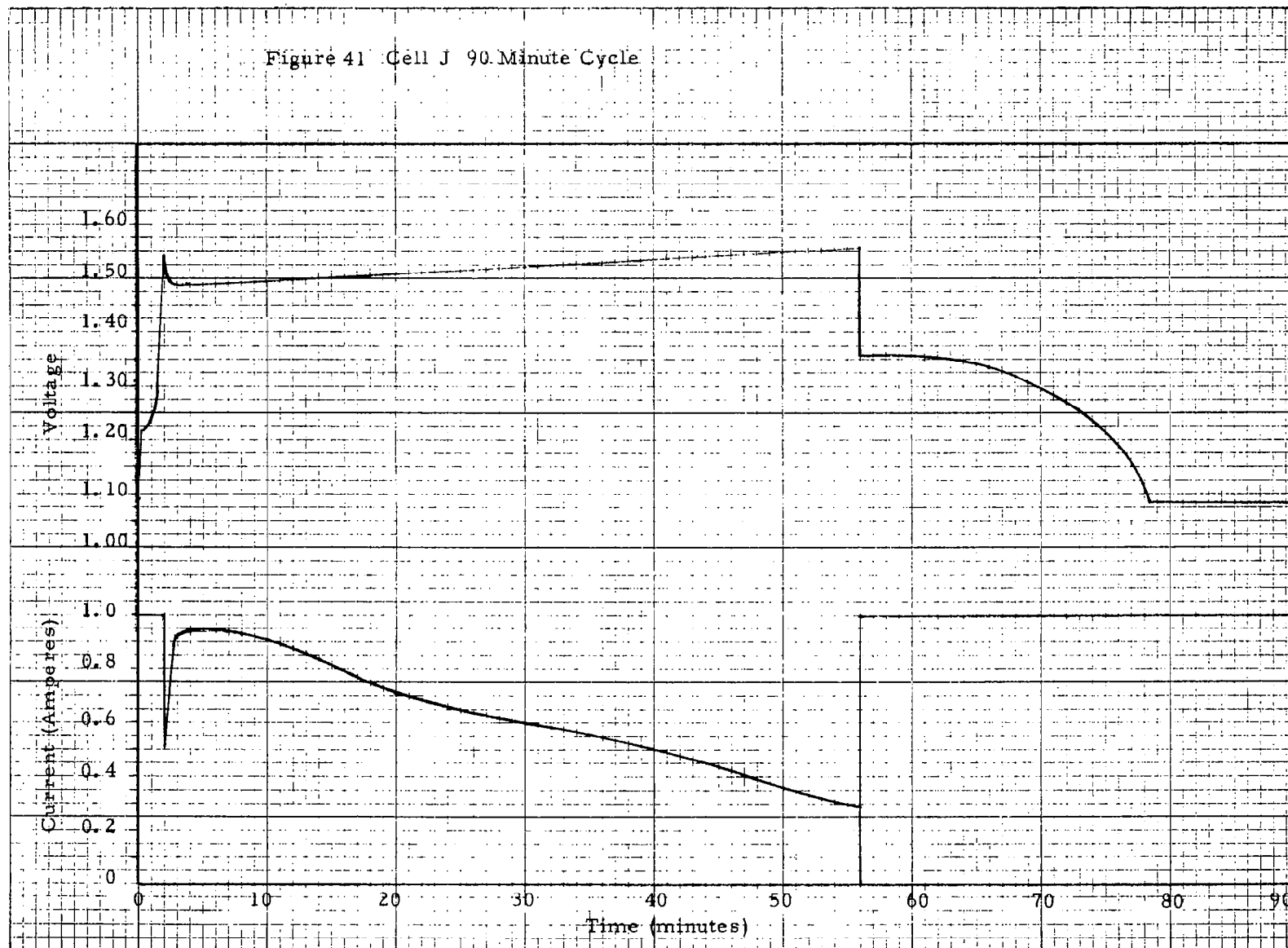


Figure 42 Cell J, 3 Hour Cycle

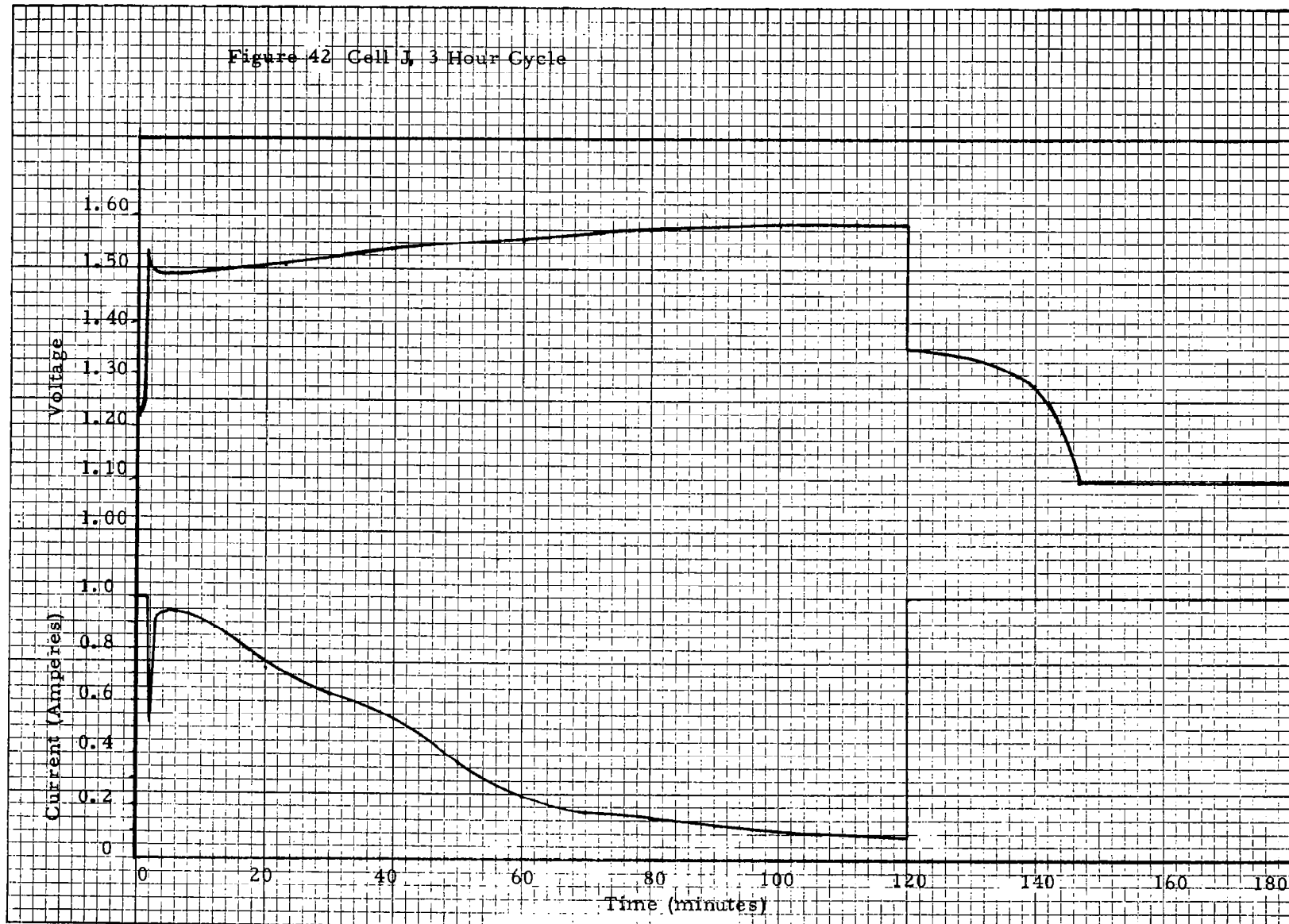


TABLE XXVIII

CYCLE SCHEDULE, CELLS J, L AND M

	<u>No. Cycles/ Day</u>	<u>CP Charge Time</u>	<u>Discharge</u>		<u>Total Cycles</u>
			<u>Time</u>	<u>Current</u>	
Cell J	16	55	35	1.0	124
	14	55	35	1.0	84
	1	120	60	1.0	<u>6</u>
					214
Cell L	14	55	35	1.0	247
	1	120	60	1.0	18
	Manual	-	-	1.5	<u>3</u>
					268
Cell M	14	55	35	1.0	137
	1	120	60	1.0	11
	Manual	-	-	1.5	2
	6	150	90	1.5	18
	6	135	105	1.5	<u>30</u>
					198

After 214 cycles, the cell was taken apart to determine the condition of the internal components. Of particular interest was the condition of the membrane seal around the positive plates. The spacer rings were slightly undersize on cell J, which provided a minimum compression of the membrane layers. The only evidence of silver migration was in one area in which the surface irregularity of a ring provided no seal.

Cell K: This cell was manually cycled to assure proper initial operation. However, due to its undesirable construction features from the manufacturing point of view, it was not placed on automatic cycling.

Cell L: This cell was cycled alternately with cell M. Cycle schedules are shown in Table XXVIII.

Cell M: This cell was cycled for a total of 148 cycles at the rate of fourteen 90-minute cycles and one 180-minute cycle per day. The charge was at 1.56 volts constant potential with a 1.0 ampere current limit; the discharge was 1.0 ampere constant current. The cell was then manually cycled to determine its effective capacity. After this, a 4 hour cycle was used which was a 150-minute constant potential charge, and a 90-minute 1.5 ampere constant current discharge. After this, the cycle times were changed to 135-minute charge, and 105-minute discharge, still at 1.5 ampere constant current. This represented a fairly severe cycle. Typical performance curves of cell M are presented in Figures 43 and 44.

Prototype Cells P1 Through P5: These cells were manually cycled at increasing rates of discharge until sufficient capacity had developed to permit automatic cycling. The cells were series connected and charged at 7.80 volts constant potential with a 5.0 ampere current limit. Discharge was through a fixed resistance of 1.21 ohms. The 90-minute cycle was 55 minutes' charge/35 minutes for a total of 16 cycles per day. A typical current curve is shown in Figure 45.

Figure 43: Cell M, Typical Voltage Curve, 3 Hour Cycle

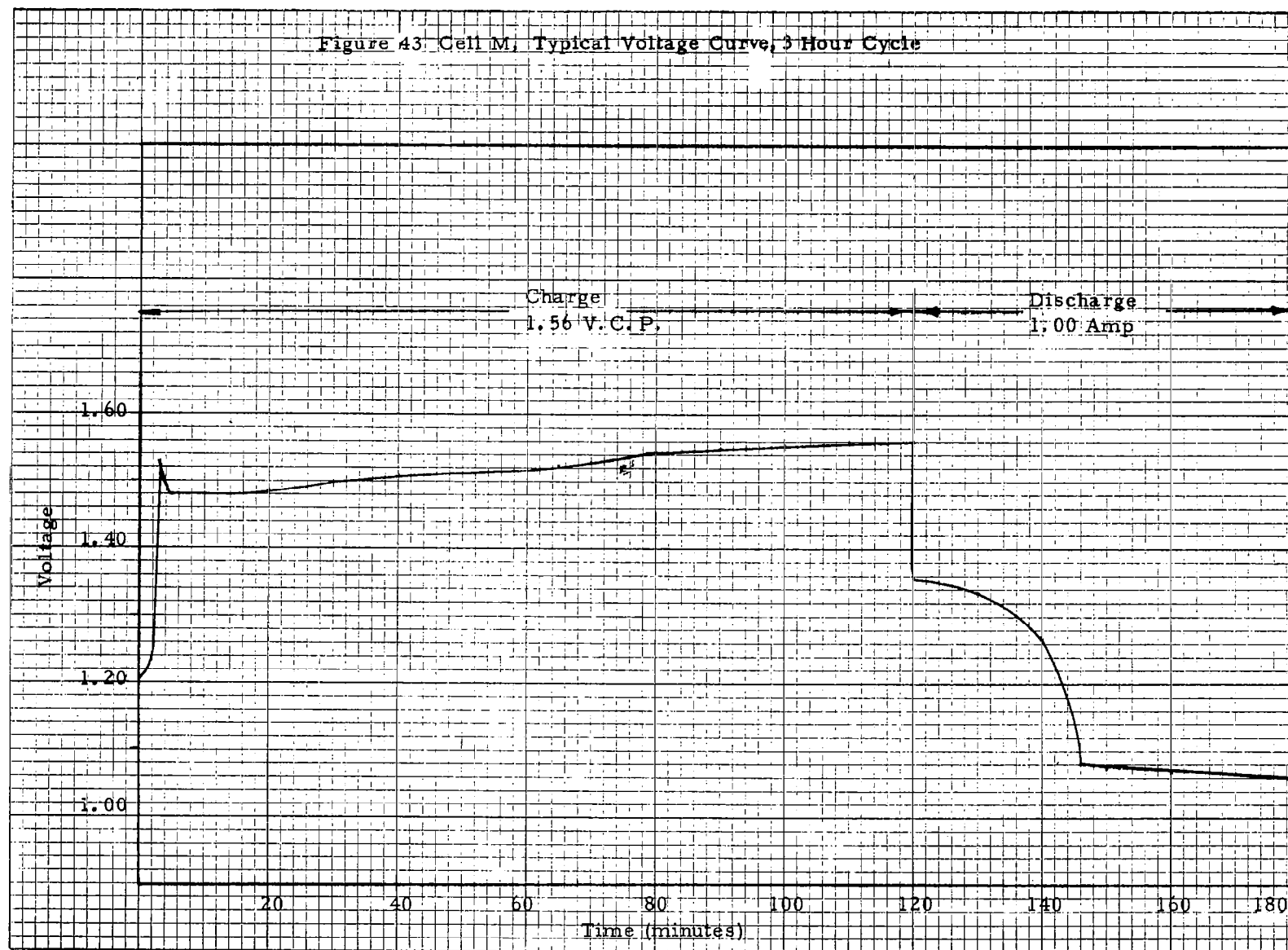


Figure 44 Cell M, Typical Voltage Curve, 4 Hour Cycle

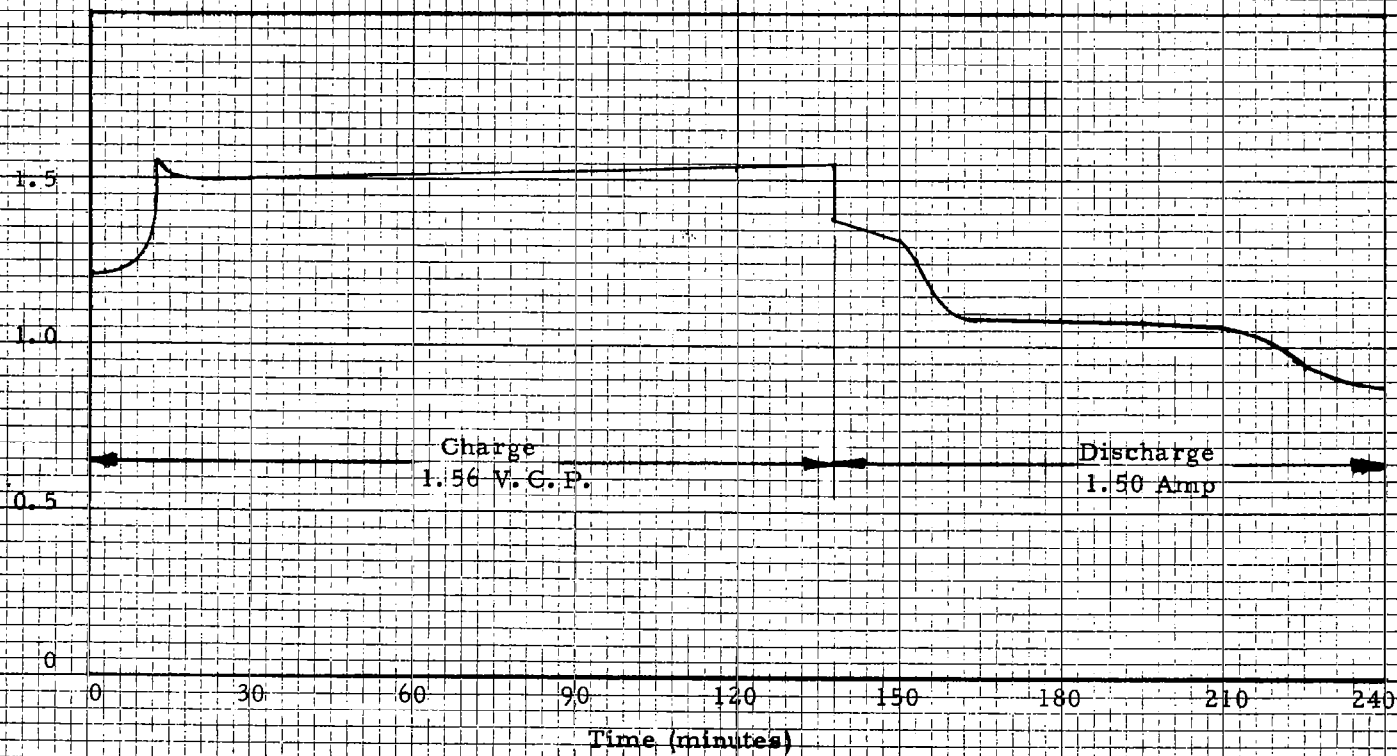
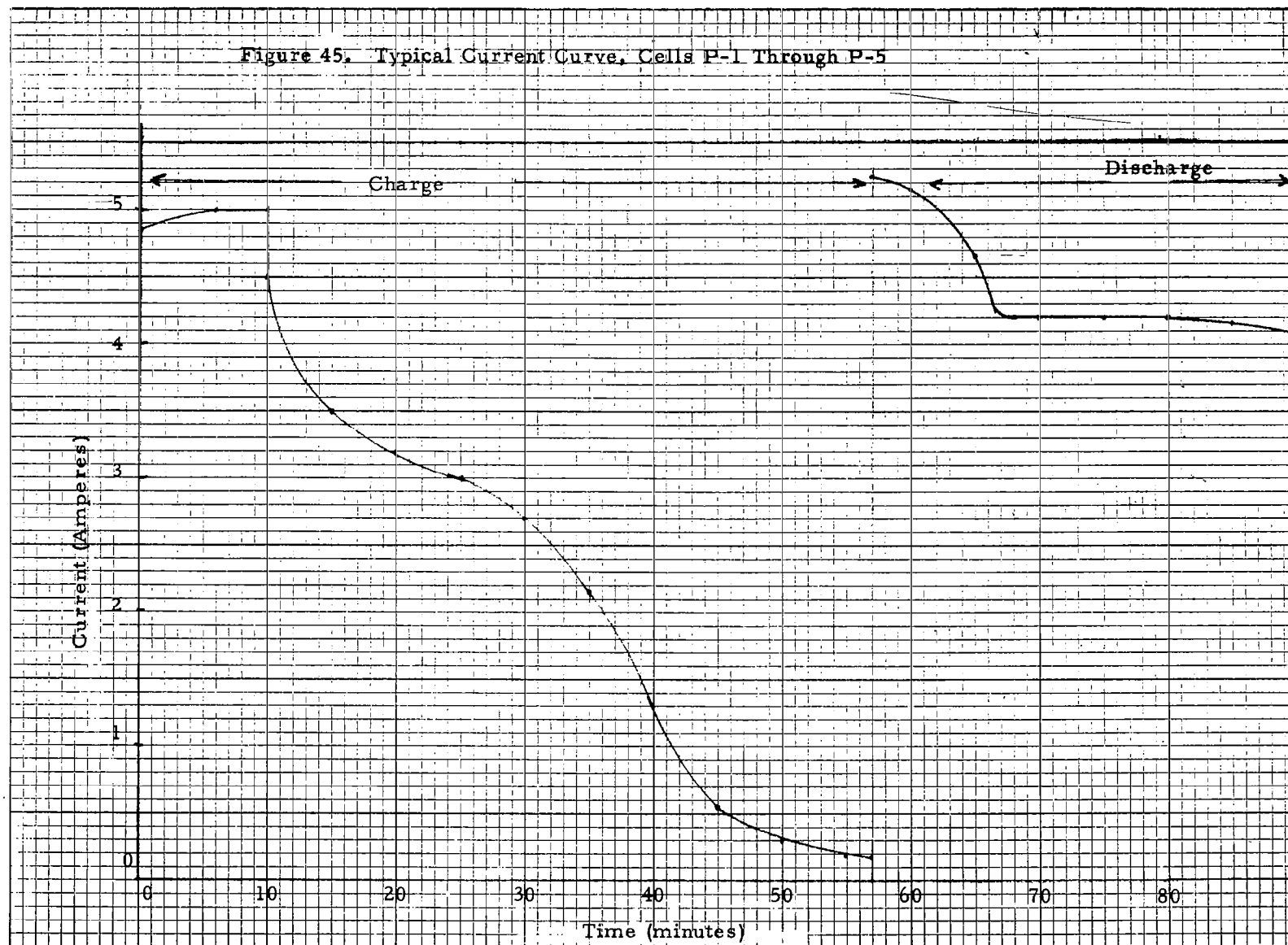


Figure 45. Typical Current Curve, Cells P-1 Through P-5



VIII. SUMMARY AND CONCLUSIONS - PHASE II

The significant problems encountered in the bipolar plate studies were the lack of charge acceptance, as well as the high degree of self discharge exhibited by the plate.

Of the several separator systems which were tested with regard to their effectiveness in withholding or preventing the migration of silver within the cells, two materials were found to be more effective in this regard, and to have other advantageous properties than those which have been used in prior cells. These are Permion 300 and 600 manufactured by Radiation Applications, Incorporated.

The effectiveness of the negative plate material was demonstrated by the successful cycling of numbers of test cells for over 700 cycles under severe conditions of charge and discharge without any failures that could not be directly attributed to malfunctions of the cycling equipment. Its effectiveness was additionally demonstrated in the cycling of the five prototype round cells through 500 cycles.

PHASE III
PROTOTYPE FABRICATION AND TESTING

IX. FABRICATION OF CELLS

A. Design Considerations

The design of cell components for Phase III was an extension of the design of cell M and the prototype cells P1 - P5 of the Phase II effort. The discussion which follows touches on the design parameters employed in Phase III, and these features are summarized in Table XXIX.

Cell Case: The cell case was of injection molded styrene-acrylonitrile with slots molded for terminal connections plus a 1/8 inch diameter fill port. Cell case components were a flat cover and a fill port plug, both injection molded of styrene-acrylonitrile. The outer dimensions were a 3.0 inch diameter by 0.67 inch length, yielding an internal volume of 4.2 cubic inches.

Element Design: The element consisted of five positive plates and six negative plates, with a combination separator system of Permion 300 and 600 plus wicks on each plate. The positive plate was of 2/0 expanded silver laminated between two layers of resin bonded silver powder sheets. The average thickness of the positive plates, after sintering and prior to formation, was 0.0125 inch. The plate area was 4.0 square inches. The average theoretical capacity of the positive plate was 98.8 ampere-minutes.

The negative plate was a pasted construction using an active material composition of 85% cadmium metal powder, 10% cadmium hydroxide, and 5% silver oxide (Ag_2O), applied to a 5/0 expanded metal base. The average thickness was 0.021 inch, with the area and configuration identical to the positive. The theoretical capacity of the negative plate was 107 ampere-minutes based on the total cadmium content of the active material.

The separator system, from positive to negative, consisted of: One layer of non-woven dynel, EM 341; one layer of modified polyethylene, Permion 300; four layers of modified cellophane, Permion 600; and one layer of non-woven dynel, EM 341. The properties of these materials have been discussed under Section VI. C.

TABLE XXIX

CONSTRUCTION DATA FOR PROTOTYPE CELL

Cell	Figures 38 and 46	
Overall Dimensions		
Weight	inch	2.83
Width	inch	3.02
Length	inch	0.67
Element		
Plates, total number		11
Dimensions, height x width	inch	1.97 x 2.38
area	sq. in.	4.0
Separator System (+ to -)	layer	1 - EM 341 dynel
	layer	1 - Permion 300
	layer	4 - Permion 600
	layer	1 - EM 341 dynel
<u>Positive Plate</u>	number	5
Type		Sintered and formed silver
Measurements before formation		
Active material, Ag*	g/plate	3.28
Plate weight	gram	4.34
Plate thickness	inch	0.0125
<u>Negative Plate</u>		
Type		Pasted
Active material composition		
Cd metal powder	% by wt.	85
CdO	% by wt.	10
Ag ₂ O	% by wt.	5
Cadmium content	g/plate	3.75
Plate weight	gram	5.16
Plate thickness	inch	0.021
Electrolyte, KOH Concentration	% by wt.	40
Volume	ml	20
Cell Capacity		
Theoretical negative group	amp-hours	8.9
Theoretical positive group	amp-hours	8.15

*Excluding weight of Exmet

The positive plate was made as a heat sealed envelope consisting of dynel and Permion 300. This was packed between eight layers of Permion 600 which were mechanically sealed by means of compression rings. The negative plate was heat sealed in a dynel envelope, and was centered between the compression rings.

The silver wire plate leads were twisted and spot welded in the area which was positioned in the cell case slot. This was done to prevent wicking of the electrolyte in the wire bundle through the seal area. Additional sealing was provided outside the cell case by encapsulating the intercell connections with catalyzed styrene monomer cement.

Cell Capacity: The theoretical capacity of the negative group was 8.90 ampere-hours; that of the positive group was 8.15 ampere-hours. The theoretical capacities of the plate groups were calculated using five plates for the negative group as is customary in our design practice.

Details of cell construction are summarized in Table XXIX, and are shown in Figure 46.

B. Manufacturing and Cell Assembly

Positive Plates: In the manufacture of positive plates, resin bonded silver sheet of suitable size and thickness was placed onto the base material -- 2/0 Exmet. The assembled material was then placed between two Teflon sheets and inserted into a hot press, which effected the desired bonding. Upon removal from the press, and after cooling, individual plates were die-cut. The plates were then sintered to burn off the resin binder and effect bonding of the silver particles. Quality assurance provides for inspection for final thickness and weight, stains and uniformity of color, and absence of foreign particles or other contaminants.

After sintering, the positive plates were formed to AgO at a suitable low current, 0.14 - 0.15 amp per plate, in a KOH bath, after which they were thoroughly washed with deionized water, dried, and desiccated. Samples were taken, analyzed, and back discharged to insure that formation requirements had been met.

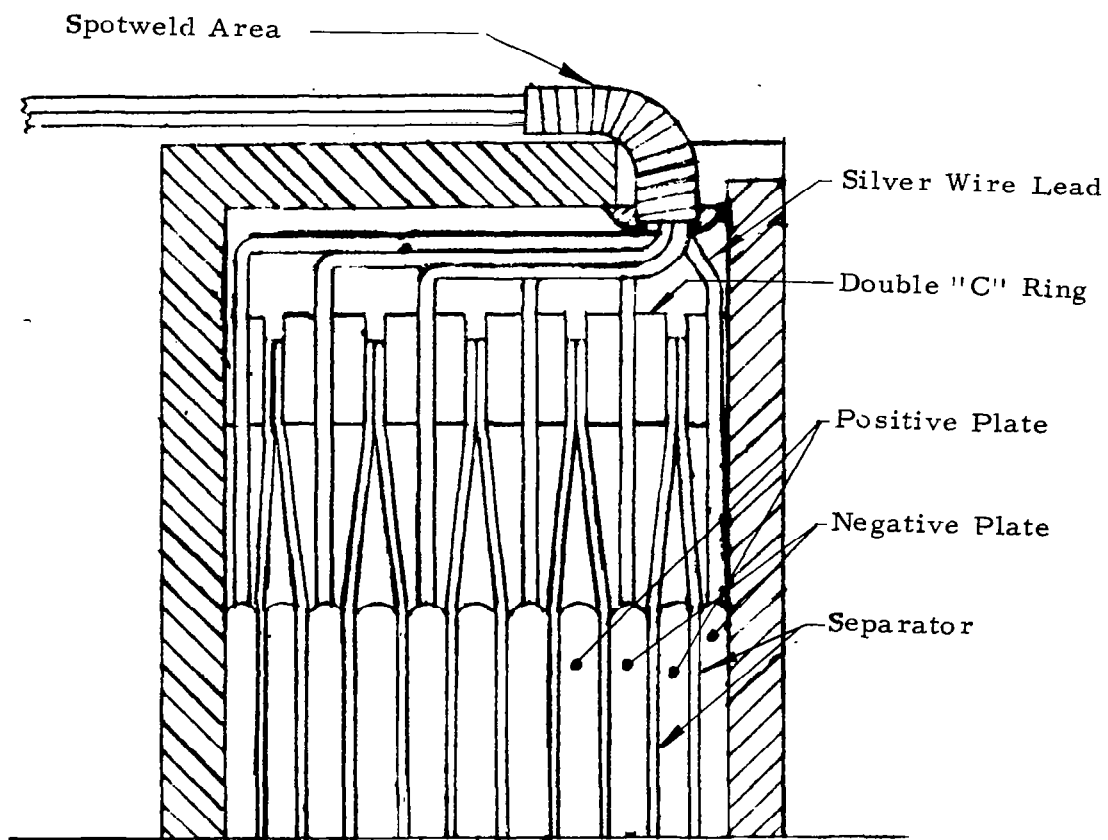


Figure 46. Final Cell Assembly

Negative Plate: The formulation of the negative plate material was held within the following limits:

<u>Material</u>	<u>Parts by Weight</u>
Cadmium Powder	85 \pm 1
Cadmium Oxide	10 \pm 0.5
Silver Oxide	5 \pm 0.5

The ingredients were thoroughly dry mixed in a mortar and pestle, after which 40 ml. of 2% polyvinyl alcohol binder were added to each 100 grams of dry mix. The paste was mixed and allowed to age for a minimum of two hours prior to application to allow the viscosity to stabilize.

Die-cut plate blanks of 5/0 Exmet, onto which tab wires had been welded, were then positioned in the plate mold. The depth of the mold setting was such as to allow for the thickness of the mold release backing paper plus the thickness of coating desired. The mold cavity was then filled with the cadmium paste which was worked through the expanded metal mesh. A straight edge was used to screed the paste, leaving a smooth surface on the coated plate. After air drying, all plates were inspected for conformity to weight and thickness requirements, as well as surface uniformity, absence of pinholes and uniform coloring.

Separators: The non-woven dynel wick and Permion 300 separators were heat sealed onto the positive plates. The positive plate envelope was then placed between two die-cut packages of Permion 600 consisting of four layers each. Doubled compression rings were positioned on the outsides of the Permion 600, then negative plates, heat sealed in EM 341, were placed between the doubled compression rings. This configuration was built up to the final element size of six negative plates and five positive plates. The separator system at this point, from positive to negative, was: One layer of non-woven dynel, one layer of Permion 300, four layers of Permion 600 and one layer of non-woven dynel.

Considerable difficulty was encountered in working with the Permion 600. This was due to variability of thickness and excessive wrinkling and brittleness of material. Rework was necessary. This involved soaking a limited amount of the material with water in order to peel it from the roll, followed by air drying under tension to remove the wrinkles. At this point, the material was rough-cut and hot pressed to remove residual moisture and gain a uniform thickness. The separator material was then mandrel wrapped, and again pressed prior to die cutting. This resulted in a uniform and smooth separator package. This problem has been discussed with the vendor and it appears that these difficulties can be overcome in the future. In the meantime, to avoid a prolonged delay of the program, it was necessary to use the available separator material.

Cell Assembly: The element was subassembled in a fixture in which the plate lead wire bundles were spot welded in the area which would lie in the cell case lead slots. The element was then transferred to the cell case, the leads potted on the inside of the case, and the cover was bonded in place with catalyzed styrene cement. The assembly was held under mechanical pressure overnight to allow for the cure of the cement. The lead wires were then potted in the spotweld area and allowed to cure. At this time, a preliminary leak check was made to determine the seal integrity.

Filling and Formation of Cells: The cells were then filled with 20 ml. of 40% KOH and given a minimum of 48 hours' wet stand. Formation of cells and subsequent balancing into batteries followed. The procedure was modified several times in order to reduce formation time and improve matching of cell characteristics.

Battery number 1, after 48 hours' wet stand, was formed by series connecting twelve cells, charging for 55 minutes at 19.1 volts (1.59 volts/cell), then manually discharging at the one amp rate. The initial discharge period was for 17 minutes to 6.0 volts. This cycling regime was continued until a discharge of one amp for 35 minutes was obtained (cycle 5), at which time the cell group was put on fully automatic cycling overnight (15 hours) (19.1 volts C. P. charge for 55 minutes/1.0 amp C. C. discharge for 35 minutes). At cycle number 14, the

discharge rate was increased to two amps; then to four amps at cycle 15; and again to the five amp discharge at cycle 17. Automatic cycling was continued at the five amp discharge rate through cycle 23. At cycle 24, the divalent silver oxide portion of the cell voltage characteristic was discharged at six amps (60 amp-minutes) for a total discharge of 180 amp minutes (see Figure 47). The cell group was then charged (cycle 25), and eleven cells were vacuum sealed as follows:

1. The cell was placed in a vacuum chamber in which provisions were made for gas inlet and mechanical seal plug manipulator as well as connection to a vacuum pump.
2. A bead of catalytic styrene cement was placed around the edge of the fill port.
3. The seal plug was placed in the holder and positioned over the fill port.
4. The atmospheric pressure in the cell and chamber was reduced to less than 20" Hg vacuum.
5. A 10-90 mixture of helium and nitrogen gases was then admitted to restore normal pressure.
6. Steps 4 and 5 were repeated an additional two times to insure the replacement of entrapped air within the cell.
7. The pressure was then reduced to a vacuum of 20" Hg (approximately 3 psia) and the seal plug seated under mechanical pressure.
8. Normal atmospheric pressure was then restored within the chamber and the cell removed and placed in a clamp to permit full setting of the cement. Pressure differential across the plug prevented loosening during the brief time of no mechanical pressure.

Upon completion of the cure of the cement, the cells were leak checked by the use of a Consolidated Electrodynamics Corporation Type 24-120 Helium Leak Detector. The cells were then cemented together in the final battery configuration.

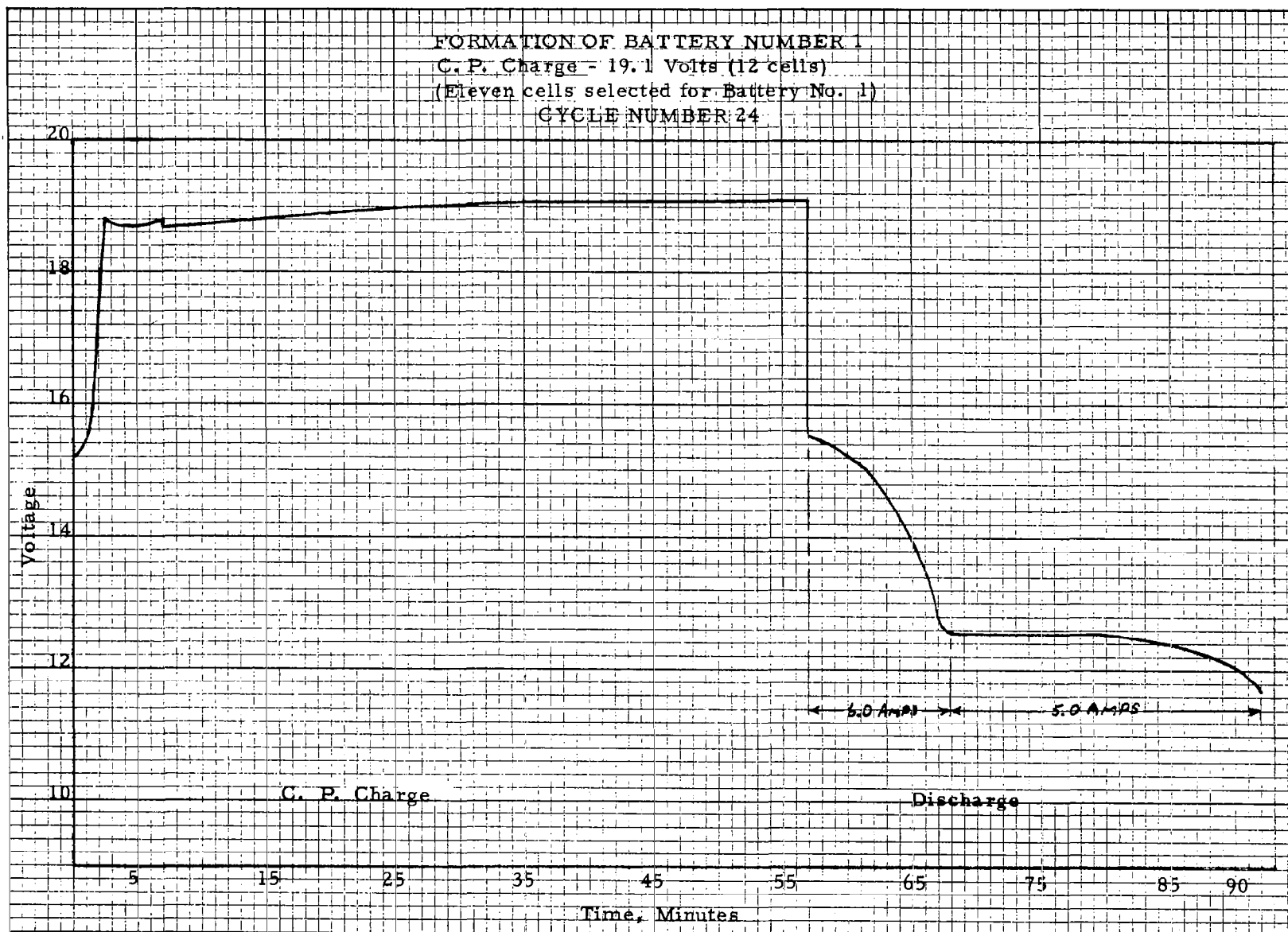


FIGURE 47

At this point, the cells were balanced by being given a parallel charge at 1.58 volts C. P. and 1.5 amp current limit, to an end point of 0.25 amp. Intercell connections, potting, etc., were then completed and the battery was taken to Narmco Research and Development Division for winding of the battery case. This battery was tested, and the data is presented in a later section of this report.

It was decided that the above formation and balancing procedures provided insufficient individual cell data for proper cell matching, therefore, the following procedures were employed for the cells to be used in Battery number 2:

Formation Procedure

1. Forty-eight hour wet stand after addition of KOH.
2. Constant potential charge in series at $1.60 \pm .02$ volts/cell with a current limit of four amps. Record voltage on each cell every five minutes.
3. Cut off charging when any cell reaches 1.60 volts. Record time from start of charging.
4. Discharge in series at $1.0 \pm .05$ amps constant current. Record voltage on each cell every five minutes until any cell reaches 0.6 volts. Record time from start of discharge.
5. Continue this cycling procedure until all cells exhibit a minimum voltage of 0.6 volts/cell at 35 minutes.
6. Repeat the above procedure except at a $2.0 \pm .05$ amp discharge rate until all cells exhibit a minimum voltage of 0.6 volts/cell at 35 minutes.
7. Repeat the above procedure increasing the amperage in one amp steps until all cells are capable of carrying 5.7 amps discharge rate to a 0.6 volt/cell cut-off voltage at 35 minutes.

Matching Procedure

1. The cells shall be matched for building into groups of eleven cell batteries on the basis of the cell voltage at the end of the last discharge period.
2. Each group of eleven cells shall be selected to have matched capacities (amp-minutes) as closely as feasible from the largest groups of cells available.
3. The cell serial numbers and above capacity characteristics shall be recorded along with the battery serial number and maintained with the battery data package.
4. Vacuum-seal cells.
5. Cement cells together per the Engineering drawing.
6. Constant potential charge the cells in parallel at $1.58 \pm .02$ volts with a current limit of 1.5 amps until the current input stabilizes at 0.25 amps or lower.
7. Complete interconnecting the cells.
8. Complete processing of the battery.

The above procedures were followed through the following three groups of twelve cells each, from which the second prototype battery of matched cells was assembled. For cell capacities of this battery, see Table XXX.

Several difficulties were encountered using these procedures, so that it was necessary to modify them further. The most important of these considerations is the limitation imposed on the entire group by the weakest cells, i. e., the few cells which exceed specification voltages, while the remainder of the group is essentially at the plateau voltages. This can best be illustrated by following 38 cells through the formation procedure (Table XXXI). These particular cells were cycled in two groups of 19 cells each (Formation Groups 5 and 6).

Note that cell number 116 in group 5 was removed at the fourth discharge because of low capacity on discharge. This necessitated the removal of a cell in group 6 to balance the voltages across the two groups. Cell number 104 was selected, since it had been exceeding 1.60 volts on charge.

TABLE XXX

CELL CAPACITIES OF BATTERY NUMBER 2:
4 AMP C. C. DISCHARGE TO 0.60 V/CELL

<u>CELL NUMBER</u>	<u>AMPERE-MINUTES</u>
28	203
34	197
41	203
42	203
47	200
48	203
49	199
51	203
56	195
58	200
59	198

TABLE XXXI
FORMATION GROUP 5

Cycle No.	Time Min.	Cells	52	53	67	68	69	70	72	73	74	75	76	80	82	84	85	86	87	97	116
Charge 1 *	17.00	Volts	1.58	1.58	1.58	1.57	1.58	1.57	1.56	1.64	1.62	1.56	1.60	1.58	1.60	1.56	1.60	1.54	1.56	1.58	-
Discharge 1 (1.0 amp)	15.00		1.31	1.31	1.30	1.28	1.28	1.30	1.30	1.28	1.28	1.28	1.30	1.28	1.30	1.28	1.28	1.30	1.24	1.26	1.30
	41.00		1.18	1.14	1.10	1.10	1.10	1.10	1.10	1.10	1.14	1.10	1.13	1.10	1.13	1.12	1.11	1.14	1.10	1.10	0.75
	42.92		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20
Charge 2	2.00		1.58	1.58	1.58	1.57	1.59	1.58	1.58	1.58	1.59	1.59	1.58	1.58	1.58	1.58	1.57	1.58	1.56	1.57	1.58
	20.00		1.58	1.59	1.60	1.60	1.60	1.60	1.58	1.58	1.66	1.64	1.56	1.62	1.60	1.64	1.58	1.64	1.54	1.56	1.61
Discharge 2 (2.0 amps)	18.00		1.08	1.08	1.08	1.08	1.08	1.08	1.07	1.07	1.06	1.06	1.07	1.06	1.07	1.08	1.08	1.07	1.08	1.08	1.04
	22.00		1.06	1.06	1.05	1.04	1.06	1.04	1.06	1.06	1.04	1.04	1.05	1.05	1.06	1.06	1.07	1.06	1.06	1.07	0.20
Charge 3	3.00		1.59	1.59	1.59	1.58	1.59	1.58	1.58	1.58	1.60	1.59	1.58	1.60	1.58	1.58	1.57	1.60	1.58	1.58	1.60
	20.50		1.58	1.58	1.58	1.58	1.58	1.58	1.58	1.58	1.57	1.60	1.56	1.61	1.60	1.60	1.58	1.60	1.54	1.55	1.59
Discharge 3 (2.0 amps)	20.00		1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.07	1.07	1.08	1.06	1.08	1.08	1.08	1.08	1.08	1.08	1.04
	25.00		Missed readings due to cell number 116								-	-	-	-	-	-	-	-	-	-	0.20
Charge 4	5.00		1.57	1.58	1.58	1.56	1.57	1.56	1.58	1.58	1.59	1.58	1.58	1.58	1.58	1.58	1.57	1.58	1.56	1.56	1.59
	23.00		1.58	1.58	1.58	1.58	1.59	1.56	1.56	1.62	1.61	1.61	1.57	1.60	1.60	1.61	1.58	1.60	1.54	1.56	1.60
			Removed cell number 116 (see cell number 104, group 6)																		
Discharge 4 (2.0 amps)	21.00		1.08	1.07	1.07	1.08	1.07	1.08	1.08	1.08	1.08	1.06	1.08	1.06	1.08	1.08	1.08	1.07	1.08	1.08	X
	34.00		1.08	1.06	1.06	1.03	1.04	1.02	1.06	1.06	1.05	1.02	1.04	1.06	1.06	1.07	1.08	1.06	1.08	1.08	-
	37.83		Re: Cell number 81, group 6																		
Charge 20	1.00		1.57	1.42	1.58	1.58	1.58	1.57	1.58	1.56	1.56	1.57	1.56	1.56	1.56	1.55	1.55	1.56	1.56	1.56	X
	42.00		1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.58	1.57	1.56	1.58	1.57	1.58	1.56	1.56	1.56	1.56	1.58	-
	56.00		1.58	1.56	1.58	1.60	1.60	1.64	1.59	1.68	1.58	1.60	1.70	1.56	1.62	1.58	1.60	1.56	1.56	1.58	-
Discharge 20 (5.7 amps)	8.00		1.11	1.04	1.06	1.04	1.04	1.06	1.04	1.02	1.04	1.04	1.04	1.02	1.04	1.04	1.04	1.04	1.04	1.02	-
	21.00		0.98	0.96	0.96	0.89	0.94	0.93	0.93	0.91	0.96	0.92	0.92	0.94	0.92	0.94	0.98	0.94	0.93	0.92	-
	22.83		-	-	-	.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Charge 21	5.00		1.51	1.52	1.52	1.52	1.52	1.52	1.52	1.53	1.52	1.52	1.52	1.52	1.52	1.51	1.50	1.51	1.51	1.52	X
	43.00		1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.56	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.56	-
	65.00		1.60	1.57	1.57	1.65	1.58	1.62	1.56	1.66	1.56	1.58	1.66	1.58	1.60	1.60	1.58	1.58	1.56	1.62	-
Discharge 21 (5.7 amps)	9.00		1.06	1.04	1.05	1.04	1.04	1.05	1.04	1.02	1.04	1.05	1.04	1.04	1.04	1.05	1.04	1.04	1.04	1.03	-
	23.00		1.04	1.03	1.04	1.02	1.02	1.04	1.02	1.00	1.03	1.03	1.02	1.02	1.02	1.03	1.03	1.02	1.02	1.00	-
	28.83		-	0.60	-	0.62	-	-	-	-	-	-	-	X	-	-	-	-	-	-	-
			Removed cells 53, 68, 80 (Re: group 6)																		
Charge 23	10.00		1.50	X	1.50	X	1.50	1.50	1.50	1.51	1.50	1.50	1.51	X	1.51	1.50	1.50	1.50	1.50	1.51	X
	157.00		Charge out overnight -- continued at 200 ma for a total charge time of 157 min.																		
			1.64	X	1.66	X	1.66	1.52	1.62	1.50	1.57	1.64	1.52	X	1.64	1.54	1.66	1.54	1.58	1.67	X
Discharge 23 (5.7 amps)	7.00		1.04	X	1.02	X	1.02	1.04	1.02	1.02	1.02	1.02	1.03	X	1.01	1.03	1.01	1.02	1.04	1.02	X
	28.00		1.00	X	.98	X	.98	1.00	.98	.97	.98	.98	.99	X	.94	1.00	.98	1.00	.98	.98	X
	33.75		.90	X	.82	X	.86	.88	.82	.81	.82	.81	.83	X	.60	.88	.82	.87	.81	.81	X
			Group 5 sent to cell assembly for sealing plugs																		

* Group 5 received nine preliminary charge cycles, from 3.83 min. to 15.0 mins., at 30.4 volts C. P. and nine discharge cycles up to 27.0 amp-minutes

TABLE XXXI (Continued)

FORMATION GROUP 6

Cycle Number	Time, Min.	Cells	79	81	83	89	90	111	92	93	94	95	96	100	101	102	103	104	105	98	99
Charge 1	17.30	Volts	1.66	1.58	1.60	1.56	1.56	1.54	1.57	1.54	1.59	1.56	1.54	1.62	1.60	1.67	1.66	1.70	1.57	1.55	1.56
Discharge 1 (1.0 amp)	17.00		1.31	1.30	1.30	1.28	1.28	1.28	1.30	1.24	1.30	1.29	1.25	1.32	1.32	1.32	1.31	1.30	1.30	1.24	1.28
	42.92		1.18	1.10	1.12	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.20	1.16	1.18	1.11	1.16	1.10	1.10	1.10
Charge 2	3.00		1.58	1.58	1.58	1.56	1.58	1.57	1.58	1.56	1.58	1.57	1.56	1.58	1.58	1.58	1.58	1.58	1.56	1.57	1.57
Discharge 2	20.00		1.70	1.60	1.64	1.56	1.56	1.54	1.58	1.54	1.64	1.56	1.54	1.67	1.65	1.70	1.56	1.62	1.58	1.56	1.56
	19.00		1.06	1.06	1.06	1.08	1.08	1.07	1.08	1.08	1.06	1.07	1.07	1.06	1.06	1.06	1.06	1.04	1.06	1.06	1.08
	22.00		Missed readings due to cell number 116																		
Charge 3	5.00		1.59	1.60	1.60	1.58	1.58	1.57	1.58	1.56	1.59	1.57	1.58	1.60	1.00	1.59	1.58	1.60	1.58	1.58	1.57
Discharge 3 (2.0 amp)	20.30		1.62	1.60	1.60	1.56	1.56	1.57	1.57	1.54	1.60	1.56	1.54	1.61	1.60	1.60	1.58	1.62	1.58	1.56	1.56
	22.00		1.08	1.08	1.06	1.08	1.08	1.07	1.06	1.08	1.08	1.06	1.08	1.08	1.07	1.06	1.08	1.07	1.04	1.07	1.08
	25.00		Missed readings due to cell number 116																		
Charge 4	7.00		1.58	1.60	1.58	1.58	1.58	1.57	1.58	1.56	1.58	1.57	1.56	1.58	1.59	1.58	1.58	1.60	1.58	1.57	1.57
Discharge 4	23.00		1.62	1.60	1.61	1.56	1.57	1.55	1.59	1.54	1.62	1.56	1.54	1.62	1.62	1.62	1.58	1.62	1.59	1.56	1.56
			Removed cell number 104 to balance with battery 5																		
Discharge 4	OC		1.42 volts on all cells				-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	23.00		1.08	1.06	1.06	1.08	1.08	1.08	1.08	1.08	1.06	1.08	1.08	1.07	1.06	1.08	1.08	X	1.07	1.08	1.08
	35.00		1.04	.94	1.03	1.00	1.02	1.01	1.05	1.00	1.03	1.04	1.03	1.04	1.01	1.06	1.00	-	1.02	.98	1.06
	37.83		-	.60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Charge 20	3.00		1.55	1.56	1.55	1.56	1.56	1.54	1.54	1.55	1.55	1.55	1.56	1.54	1.56	1.54	1.56	-	1.55	1.56	1.54
Discharge 20 (5.7 amps)	43.00		1.58	1.58	1.57	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.58	1.57	1.58	-	1.56	1.57	1.58
	57.00		1.66	1.58	1.60	1.60	1.57	1.57	1.58	1.56	1.56	1.60	1.57	1.60	1.64	1.64	1.64	-	1.57	1.58	1.60
Total time	8.30		1.04	1.02	1.03	1.04	1.04	1.03	1.04	1.04	1.03	1.04	1.02	1.04	1.01	1.03	1.01	-	1.02	1.02	1.04
	22.00		.92	.90	.92	.92	.92	.96	.90	.91	.87	.92	.91	.92	.90	.94	.84	-	.89	.83	.91
	22.83		See battery 5																		
Charge 21	5.30		1.51	1.52	1.51	1.51	1.51	1.50	1.51	1.50	1.51	1.51	1.51	1.51	1.52	1.51	1.52	-	1.52	1.52	1.51
Discharge 21 (5.7 amps)	43.00		1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.55	1.54	1.55	-	1.54	1.55	1.54
	66.00		1.62	1.60	1.58	1.58	1.60	1.57	1.56	1.58	1.58	1.58	1.58	1.60	1.60	1.61	1.64	-	1.61	1.61	1.62
Total time	11.00		1.04	1.02	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.03	1.04	1.01	1.04	1.00	-	1.02	1.02	1.04
	24.00		1.01	1.00	1.02	1.02	1.02	1.01	1.02	1.00	.99	1.02	1.00	1.00	.98	1.01	.98	-	.98	.96	1.00
	28.50		-	.64	-	-	-	-	-	-	.60	-	-	-	-	-	.58	-	Removed cells		
Charge 23	11.00		1.51	-	1.50	1.50	1.50	1.50	1.50	1.50	X	1.50	1.50	1.50	1.52	1.50	X	X	1.51	1.51	1.50
Discharge 23 (5.7 amps)	158.00		Charge out overnight -- continued at 200 ma for a total charge time of 158 min.																		
	8.00		1.54	-	1.61	1.64	1.52	1.51	1.62	1.54	-	1.66	1.52	1.65	1.63	1.64	-	-	1.51	1.62	1.62
Total time	30.00		1.02	-	1.00	1.01	1.02	1.02	1.02	1.02	-	1.01	1.02	1.01	.98	1.02	-	-	1.02	1.00	1.01
	33.45		.98	-	.96	.97	.98	.98	.98	-	-	.94	.96	.96	.94	.98	-	-	.96	.90	.96
			See battery 5																		

Again, six cells were removed at the end of discharge number 21 -- three from each group -- because they were limiting the remainder of the cells due to low capacity discharge. Formation groups -- now consisting of 15 cells each -- were sealed at the end of discharge number 23. Actually, full qualification had not been obtained due to cell number 82 in group 5 (33.75 minutes to 0.60 volt at 5.7 amps, instead of 35 minutes); however, it appeared from the voltage readings that the remainder of the cells would have qualified had cell 82 not limited them.

Another difficulty in the procedure becomes evident upon reading Table XXXI, viz., that the operator encounters great difficulty in maintaining readings as the end voltages are approached on charge and discharge. It can be seen that, in many instances, these end points were badly over-run.

During the formation cycling of groups 5 and 6, experiments were being carried out to determine the charge acceptance of cells formed in parallel. The data presented in Figures 48a - 48f indicated that the differences in charge acceptance and discharge characteristics were not great, e. g., if two cells paralleled were charged at 10 amps, one would not accept all the charge while the other received no charge. The obvious advantage is the control of the potential of all cells within the desired limits. This, of course, eliminates accidental reversal on discharge, and excessive gassing on charge. There is also the added advantage of the group not being limited by the weakest cell.

The above observations were put into practice with the cycling of Formation Group 7, which was the first parallel formed group. Figure 49 is a plot of a typical formation cycle and Table XXXII illustrates the capacity rating of the individual cells of group 7.

The procedure used for group 7 was further modified for Formation Group 8 and all subsequent groups to include basically the high charge rate portion of the curve, while eliminating the lower charge rates, until high capacity had been achieved. Following is the final procedure which was employed for the remaining batteries:

TABLE XXXII

CELL CAPACITIES OF FORMATION GROUP NUMBER 7

<u>CELL NUMBER</u>	<u>AMP-MINUTES*</u>
117	192
118	214
109	217
11	218
119	219
106	220
77	223
113	224
125	225
110	226
108	227
107	229
115	231
120	231
114	231
122	234
124	241
14	253

*4.0 amp C. C. discharge

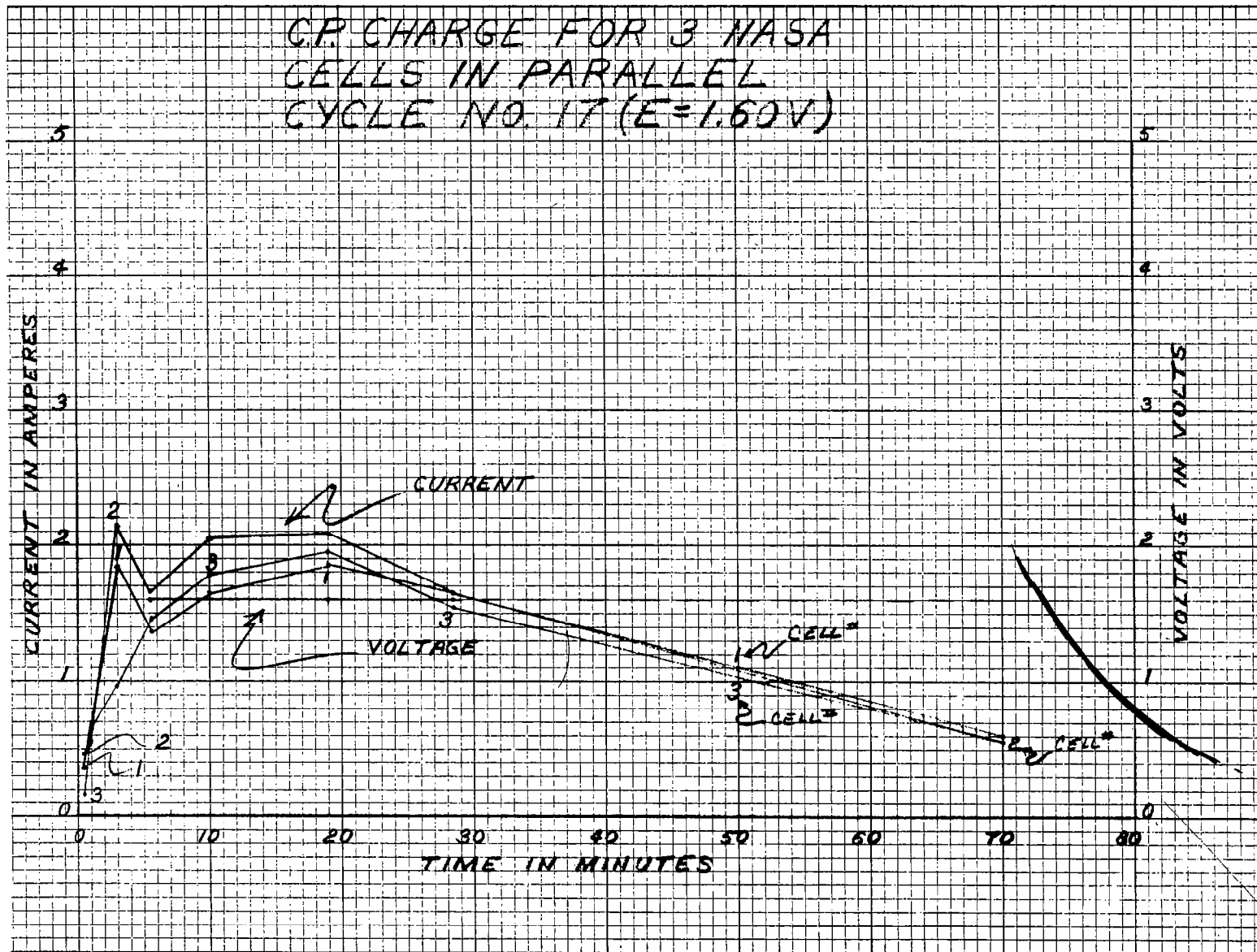


FIGURE 48a

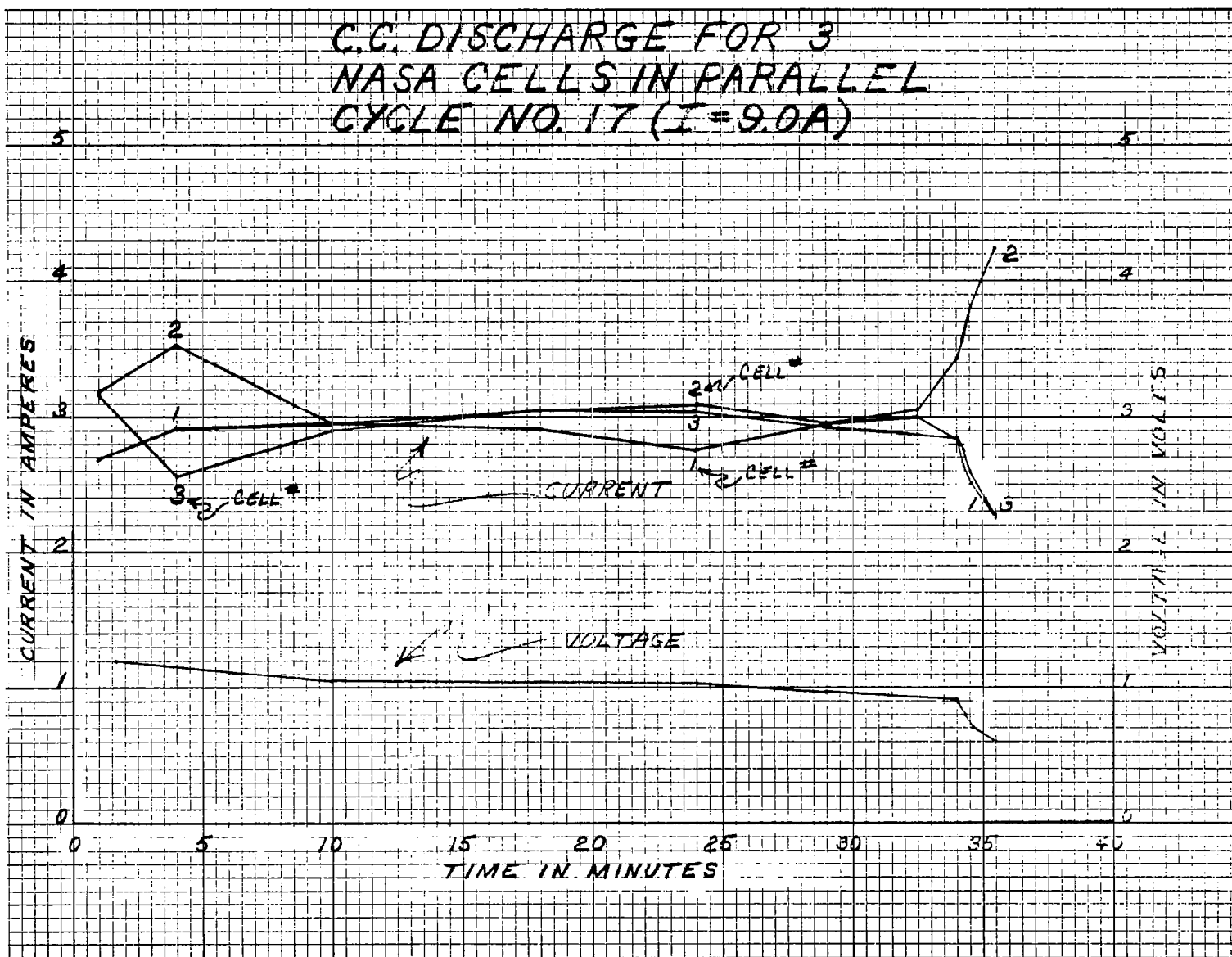


FIGURE 48b

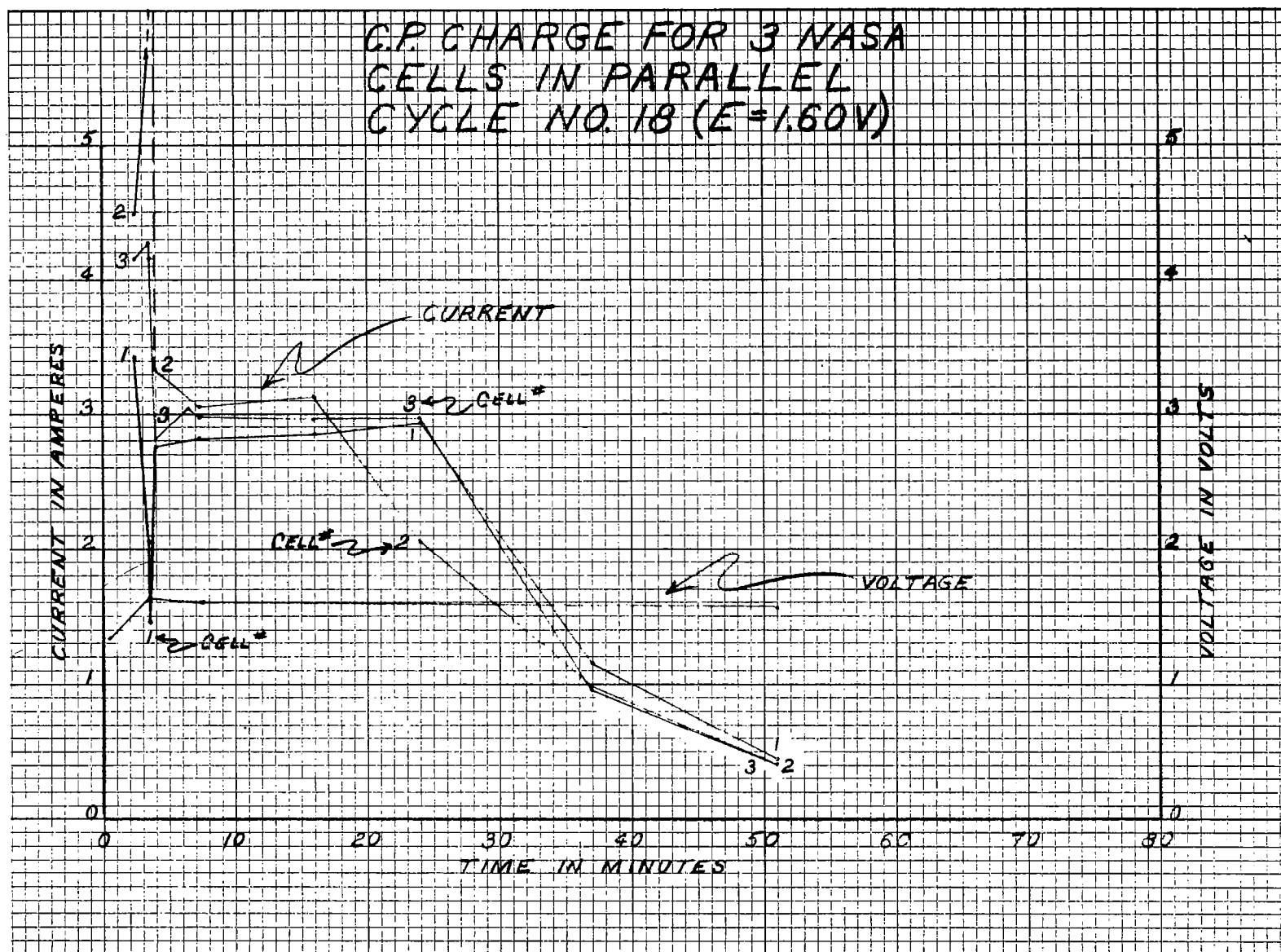


FIGURE 48c

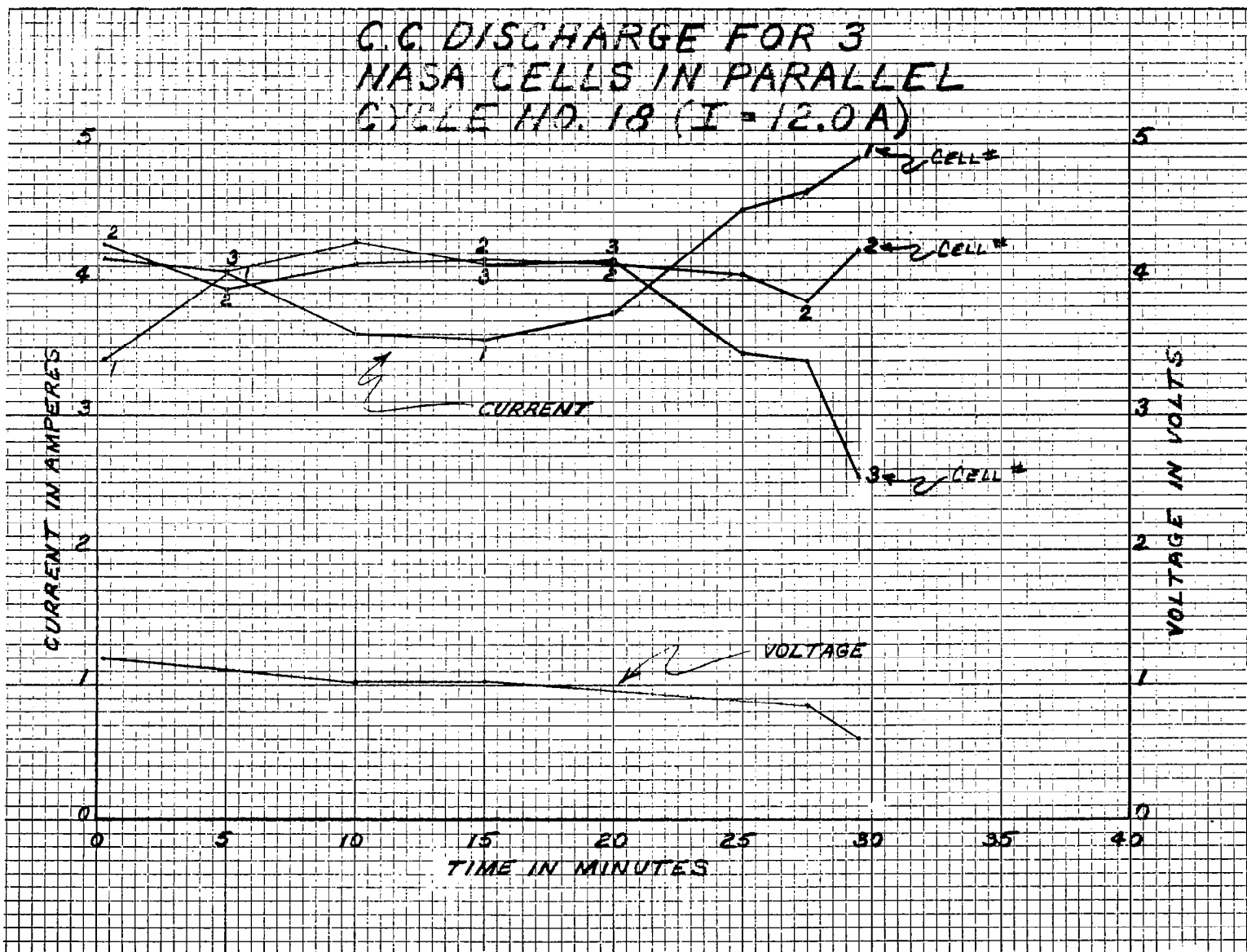


FIGURE 48d

G.P. CHARGE FOR 3 NASA CELLS IN PARALLEL CYCLE NO. 20 ($E = 1.50 \text{ V}$)

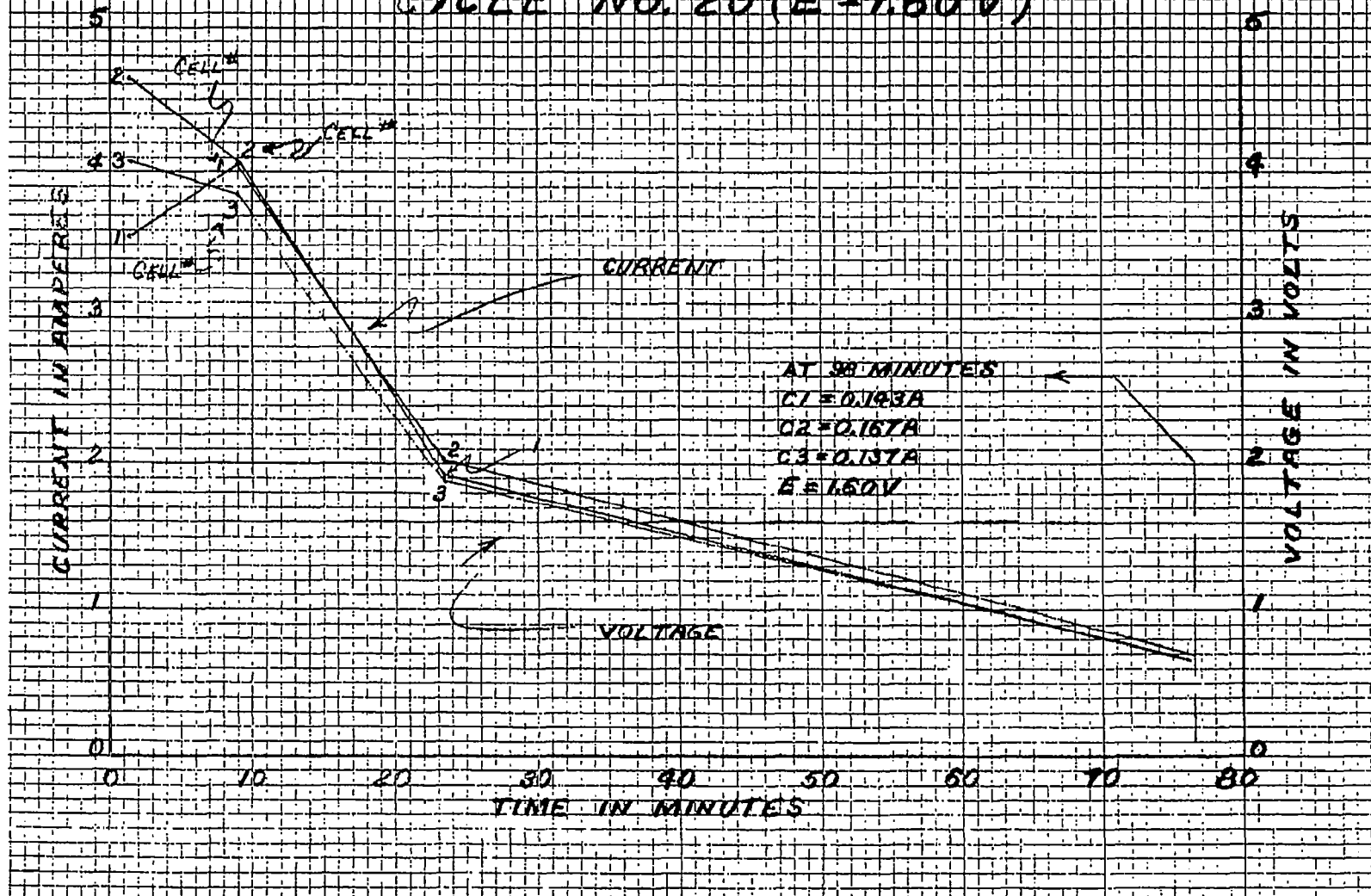


FIGURE 48e

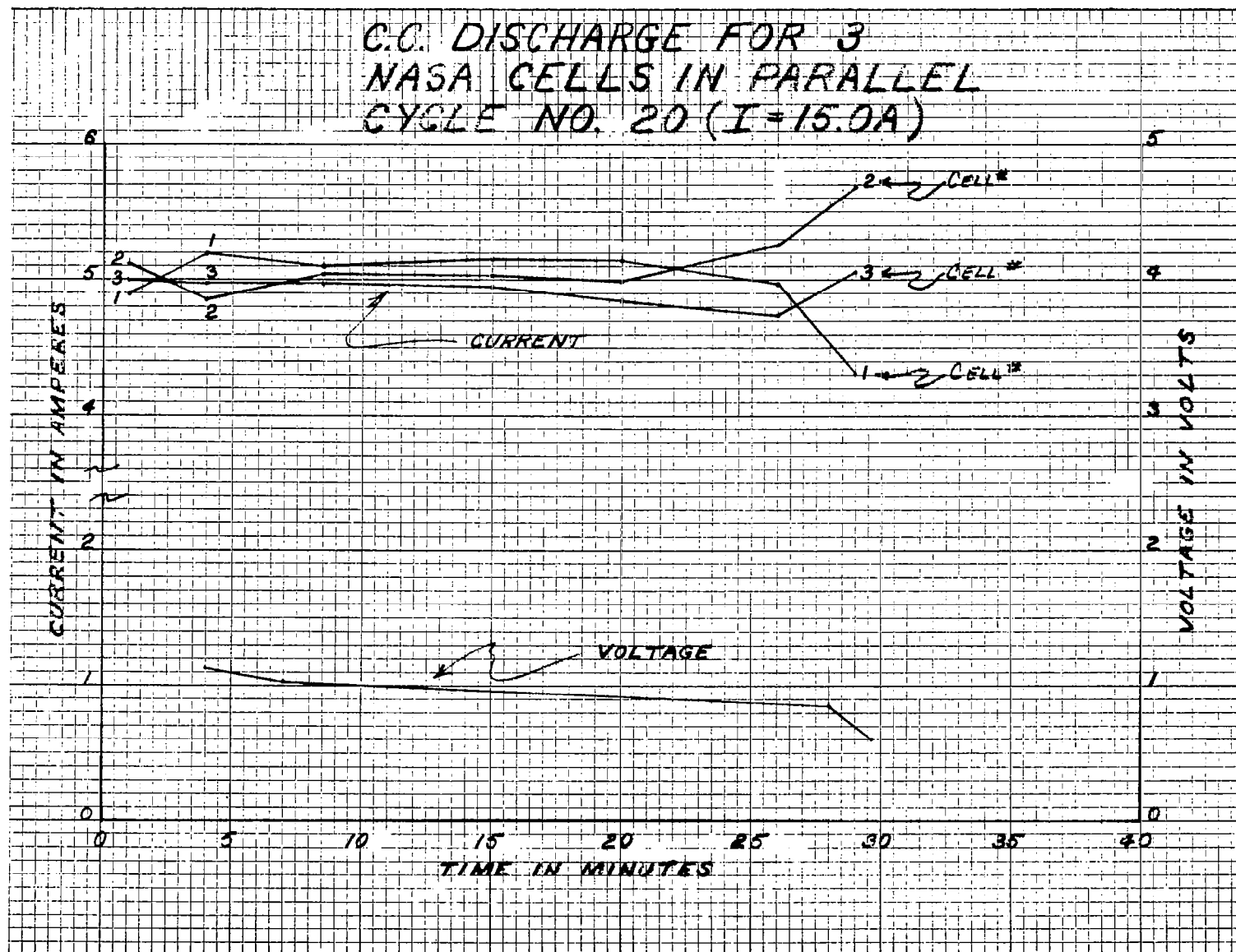


FIGURE 48f

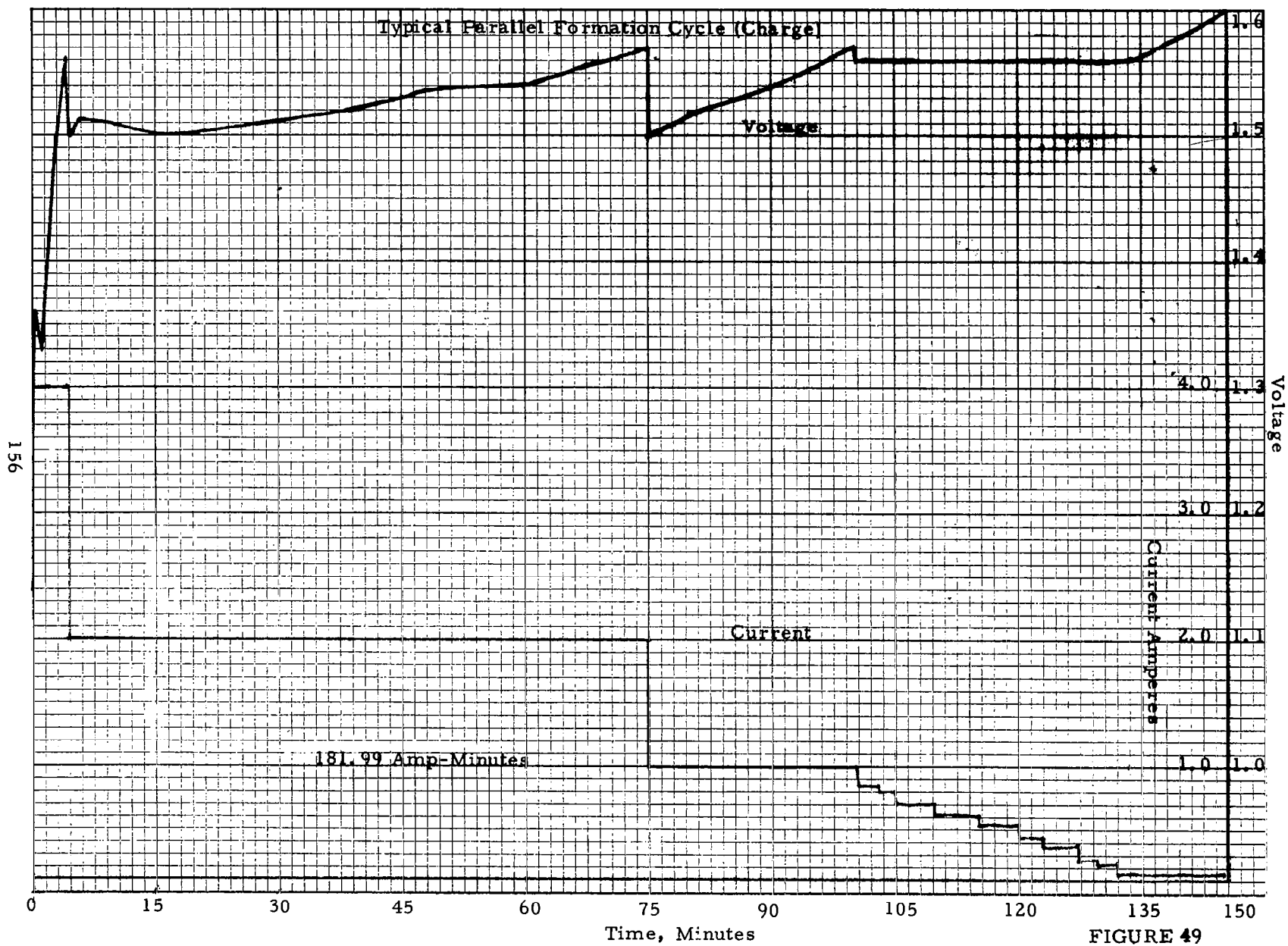


FIGURE 49

Parallel Formation Procedure

1. Forty-eight hour wet stand.
2. The initial charge cycles shall be at one amp per cell (18 amps/18 cell group) for five minutes. This will be approximately five cycles.
3. The initial discharge cycles shall be at one amp per cell until a total discharge time of greater than five minutes to 0.60 volt is obtained. This will be approximately five cycles.
4. The ensuing charge cycles shall be increased 0.5 amp per cell, maintaining a voltage less than 1.60. As the end point is reached (1.60 volts), the amperage shall be decreased by 0.5 amp per cell until an end point less than 1.60 volts at the one amp per cell rate is reached. The maximum charge time at this point shall be 15 minutes.
5. The ensuing discharge cycles shall be increased 0.5 amp per cell when the discharge time on the preceding cycle has exceeded five minutes.
6. The above charging procedure shall apply until a charge acceptance of five amps per cell for ten minutes is reached, at which time the charge cycle shall be increased to 20 minutes.
7. When the charge acceptance is greater than five amps per cell for 15 minutes, the charge cycle shall be increased to 25 minutes; the current may be reduced in increments of one amp per cell. As the charge acceptance is increased by five minutes or more, the charge cycle shall also be increased by five minutes. This is to be continued until the charge acceptance becomes five amps per cell at 35 minutes, and a total charge time of 45 minutes.
8. The maximum discharge rate shall be 5.7 amps per cell.
9. Cells shall never be left in a discharged state, and the last charge of the day shall be finished at the rate of 0.5 amp per cell to 1.60 volts.

10. When starting cells at the beginning of the shift, a float charge of 0.5 amp per cell for five minutes, or to 1.60 volts, shall be employed.
11. When cells have surpassed a discharge of 5.7 amps per cell for 35 minutes, they shall be vacuum-sealed (in the discharged state).

Cell rating results for group 7 are shown in Table XXXII. It is to be noted that, in general, the capacities developed in parallel formed groups are higher than in series formed groups. Data summarizing the build-up of capacity for Formation Group 10 is presented in Table XXXIII.

Of course, the apparent conclusion to be drawn from the above observations is that the ideal formation procedure, on the cell level, would be to cycle each cell individually. In this way, both potential and current are controlled at all times, as well as the rate of depth of discharge (and charge) of the particular cell.

After the cell groups had been formed and sealed, they were balanced into the final battery configuration by means of matching individual cell capacities. This was accomplished by first parallel charging the group and then series discharging at four amperes constant current. As the end point (0.60 volt) of a given cell was reached, it was shunted out of the group, the time was noted, and the discharge continued. Table XXXII is a listing of the capacities of the cells in group 7 which were obtained by the above procedure.

Batteries were then made by matching cells as closely as feasible from the cells available. Table XXXIV is a summary of capacities of the batteries.

As specified in the matching procedure, Batteries 1 and 2 were assembled in a charged condition. Apparently, during the spot-welding of the cell interconnectors enough shorting had occurred to leave the cells badly out of balance. It was for this reason that Battery 2 was cycled without the filament wound case, so that the individual cell voltages could be monitored. During the very early cycles, cell charge voltages ranged from 1.46

TABLE XXXIII

FORMATION GROUP NUMBER 10

<u>CYCLE NUMBER</u>	<u>CHARGE</u> (Amp-Min)	<u>DISCHARGE</u> (Amp-Min)	<u>RATE</u> (Amp)
1	5.00	5.00	1.0
2	5.00	5.63	1.5
3	5.50	6.38	1.5
4	6.25	6.00	1.5
5	6.50	7.50	1.5
6	12.00	13.38	2.0
7	14.00	14.92	2.5
8	21.25	22.83	3.0
9	23.75	25.12	3.5
10	40.13	39.37	3.5
11	38.25	40.68	4.0
12	43.00	49.12	5.0
13	51.00	58.58	5.0
14	71.25	75.32	5.0
15	71.25	79.69	5.0
16	80.00	89.75	5.0
17	91.00	99.41	5.0
18	100.00	109.42	5.0
19	120.50	124.38	5.0
20	125.00	125.34	5.0
21	123.50	136.96	5.0
22	132.50	146.25	5.0
23	142.00	147.73	5.0
24	155.50	157.26	5.0
25	174.25	179.18	5.0
26	179.00	184.10	5.7
27	173.25	179.35	5.7
28	171.00	175.20	5.7
29	198.00	198.54	5.7

TABLE XXXIV

BATTERY CAPACITIES

<u>BATTERY NUMBER 1</u>		<u>BATTERY NUMBER 2</u>	
<u>Cell Number</u>	<u>Amp-Minutes</u>	<u>Cell Number</u>	<u>Amp-Minutes</u>
1	180 amp-	28	203
2	minutes	34	197
3	nominal -	41	203
4	see Figure 1	42	203
5		47	200
6		48	203
7		49	199
9		51	203
12		56	195
15		58	200
16		59	198

<u>BATTERY NUMBER 3</u>		<u>BATTERY NUMBER 4</u>	
<u>Cell Number</u>	<u>Amp-Minutes</u>	<u>Cell Number</u>	<u>Amp-Minutes</u>
20	205	11	218
73	181	106	220
74	185	107	229
75	180	108	227
76	186	109	217
80	188	110	226
81	189	113	224
82	195	114	231
84	186	115	231
94	202	122	234
111	190	124	241

TABLE XXXIV (Continued)

<u>Battery #5</u>		<u>Battery #6</u>		<u>Battery #7</u>		<u>Battery #8</u>	
<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>
148	212	25	222	130	202	135	216
152	212	77	223	173	197	119	219
172	212	132	224	151	196	139	204
144	214	162	224	174	209	117	221
147	214	167	225	123	196	128	211
160	215	153	226	145	209	129	223
146	215	165	228	150	197	154	215
168	215	157	228	127	213	126	225
21	217	26	230	131	200	39	221
22	219	155	231	118	214	125	225
163	220	171	246	158	194	140	226

<u>Battery #9</u>		<u>Battery #10</u>		<u>Battery #11</u>		<u>Battery #12</u>	
<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>	<u>Cell</u>	<u>A-M</u>
170	249	133	220	134	218	93	199
120	231	44	219	13	222	53	184
169	232	29	219	79	216	166	200
142	236	13	222	103	222	32	195
24	237	37	227	68	210	30	184
138	238	54	244	87	226	38	180
23	239	33	255	136	216	46	180
141	243	31	232	65	204	27	186
161	245	72	213	112	203	43	187
143	246	159	214	18	202	66	187
14	253	164	223	149	202	137	194

to 1.80 volts across the battery. Four cells were above the 1.60 volt limit at 1.74, 1.76, 1.78 and 1.80. These cells cracked from gas pressure, and began to lose electrolyte. The testing was stopped on this group, and an effort was made to stop the leaks, and to rebalance the cells individually. However, due to loss of electrolyte, this battery was not returned to the test program. In view of this, it was elected to assemble the remaining cells in a fully discharged state.

This presented an additional hazard in activating the battery. It had been noted during formation cycling that the charge acceptance of cells left in the discharged state overnight was very poor the next day. For example, Formation Group 7 was left in a discharged condition over the weekend following discharge 5. The charge acceptance of cycle 5 had been 64.66 amp-minutes for 78.5 minutes, with an initial charge rate of 4.90 amps per cell. The first cycle of the following week showed a charge acceptance of 12.34 amp-minutes for 78.5 minutes, with an initial rate of 0.17 amp per cell. Reference is also made to the data for group 8, Table XXXV.

Adding to the problem of charge acceptance on activation of the battery is the fact that the matched cells were jumper discharged through a 0.4 ohm resistor overnight in parallel before being sent to final assembly. This was done to leave a small residual capacity. They then remained in this condition for about a week through the winding of the battery case. Thus far, the reactivation of the final battery has been successfully accomplished by means of several low charge rate cycles. This was done because of the known low charge acceptance of cell groups which had been noted in the parallel formation cycling, and also because of the possible variation of charge acceptances of individual cells. The procedure for activation of the batteries prior to testing is given in the next section -- Prototype Testing.

•

TABLE XXXV

LOSS OF CAPACITY - FORMATION GROUP NUMBER 8

Cell Group (18) cells) left in discharged state for 64 hours at the end of cycle number 24.

<u>CYCLE NUMBER</u>	<u>CHARGE</u> (Amp-Min)	<u>DISCHARGE</u> (Amp-Min)	<u>RATE</u> (Amp)
21	91.00	98.75	5.0
22	98.00	105.54	5.0
23	108.00	115.83	5.0
24	131.00	140.17	5.0

(Left in discharged state for 64 hours)

25	20.00	18.73	5.0
26	34.30	33.50	5.0
27	45.00	45.00	5.0
28	49.00	49.58	5.0
29	85.00	87.90	5.0
30	97.00	99.98	5.0
31	133.00	138.77	5.0

X. PROTOTYPE TESTING

It was not intended that an extensive testing program would be conducted at Power Sources. Under the terms of the contract, four batteries have been delivered to NASA for evaluation. However, some evaluation was done on single cells and on batteries. For reference, a test procedure, Power Sources Number 60219, is included in Appendix D. Following is a discussion of the testing that was done at Power Sources.

A. Single Cell Tests

Serial Number 14: This cell was evaluated for capacity at various rates of discharge. The initial formed capacity was 253 ampere-minutes at 4.0 ampere constant current discharge to a 0.60 volt end point. Subsequently, the cell was charged at 1.56 volts constant potential with a ten ampere current limit for all discharges except the one ampere. The charge for this was at 1.56 volts C. P. with a 1.50 ampere current limit. In Figure 50, a definite difference of silver (II) oxide performance is seen. The following table summarizes the results:

TABLE XXXVI

RESULTS OF CAPACITY DETERMINATIONS OF S/N 14
AT VARIOUS RATES OF DISCHARGE. ALL CHARGES
ARE 1.56 VOLTS C. P. ; ALL DISCHARGES CONSTANT
CURRENT TO 0.60 VOLTS

<u>Discharge Rate, Amps</u>	<u>AgO Capacity Amp-Min. (1)</u>	<u>Total Capacity Amp-Min.</u>	<u>Current Density Amp/in² (2)</u>	<u>Charge Current Limit</u>
1	90	298	.025	1.5
2	92	282	.05	10
4	72	250	.10	10
10	70	240	.25	10

(1) Taken as capacity to Ag₂O plateau

(2) Based on positive plate area

SILVER-CADMIUM CELL PERFORMANCE AT VARIOUS RATES OF DISCHARGE

P/N 201321

S/N 14

Room Temperature

C.P. charge @ 1.56 volts,

10 Amp current limit

- 1 Amp C.C. Discharge (1.50 amp current limit charge)
 ○ 2 Amp C.C. Discharge
 △ 4 Amp C.C. Discharge
 □ 10 Amp C.C. Discharge

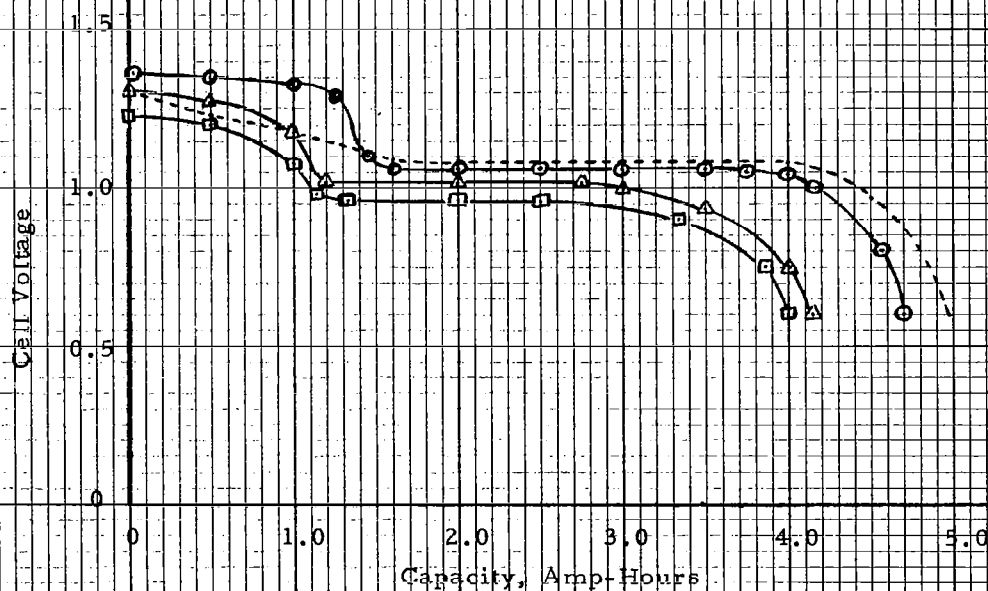


Figure 50

Figure 51 is a plot of the above capacities, referenced to the 1.0 ampere discharge as unity, versus current density.

Serial Number 45: The initial formed capacity was 238.7 amp-minutes at 4.0 ampere constant current discharge to 0.60 volt. This cell was used to evaluate temperature performance under charged storage conditions. The initial room temperature capacity determinations were made after a 16-hour 1.56 volt C. P. charge at a 1.50 ampere current limit. There was a 30-minute open circuit stand before the discharge was begun. For the remaining temperature levels, a 24-hour open circuit temperature soak was employed before the start of discharge. All discharges were run at 1.10 ampere constant current, equivalent to a current density of 0.0275 amp/square inch. The results are summarized in Table XXXVII and are plotted in Figure 52.

TABLE XXXVII

TEMPERATURE PERFORMANCE OF S/N 45:
DISCHARGED AFTER 24 HOURS' TEMPERATURE SOAK

<u>t °F</u>	<u>Amp-Min. to 0.60 volts</u>	<u>Capacity % of R. T.</u>
150	285.1	111.1
78	256.6 ⁽¹⁾	100.0
-5	203.5	79.0
-20	181.8	70.6
-40	133.8	52.0

- (1) Average of two determinations. Room temperature discharges were started after 30 minutes open circuit stand.

Serial Number 71: This cell has been cycled at a 55 minute constant potential charge/35 minute 2.0 ampere constant current discharge. To date, 1800 cycles have been surpassed, and the cell is continuing on cycle.

CAPACITY vs. CURRENT DENSITY

S/N 14

Referenced to 1.0 ampere C.C. Dis-
charge at room temperature

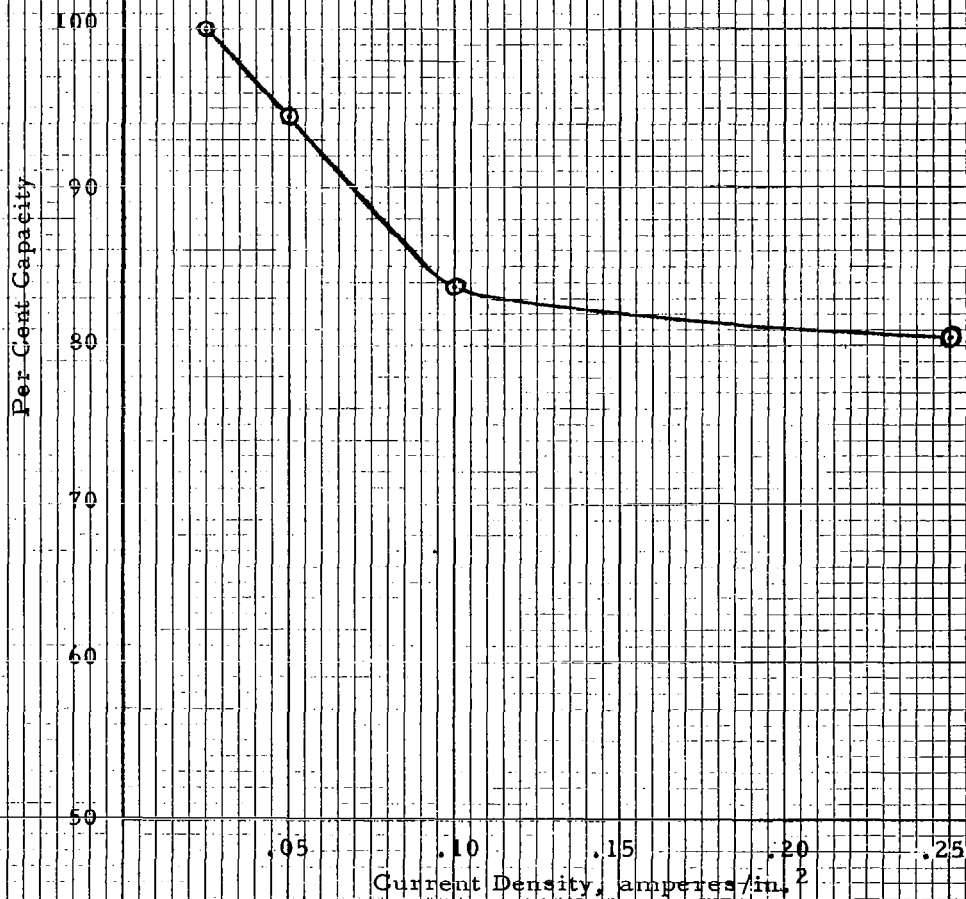


Figure 51

POWER SOURCES
DIVISION OF
TELECOMPUTING CORPORATION
DENVER, COLORADO

SILVER-CADMIUM CELL PERFORMANCE
AT VARIOUS TEMPERATURES

Cell Part Number 201321
Serial Number 45

Test Conditions:

C. P. Charge - 1.55 volts - room temperature

24 hour soak at low temperatures (open circuit) before discharge

1.10 Amp C. C. discharge

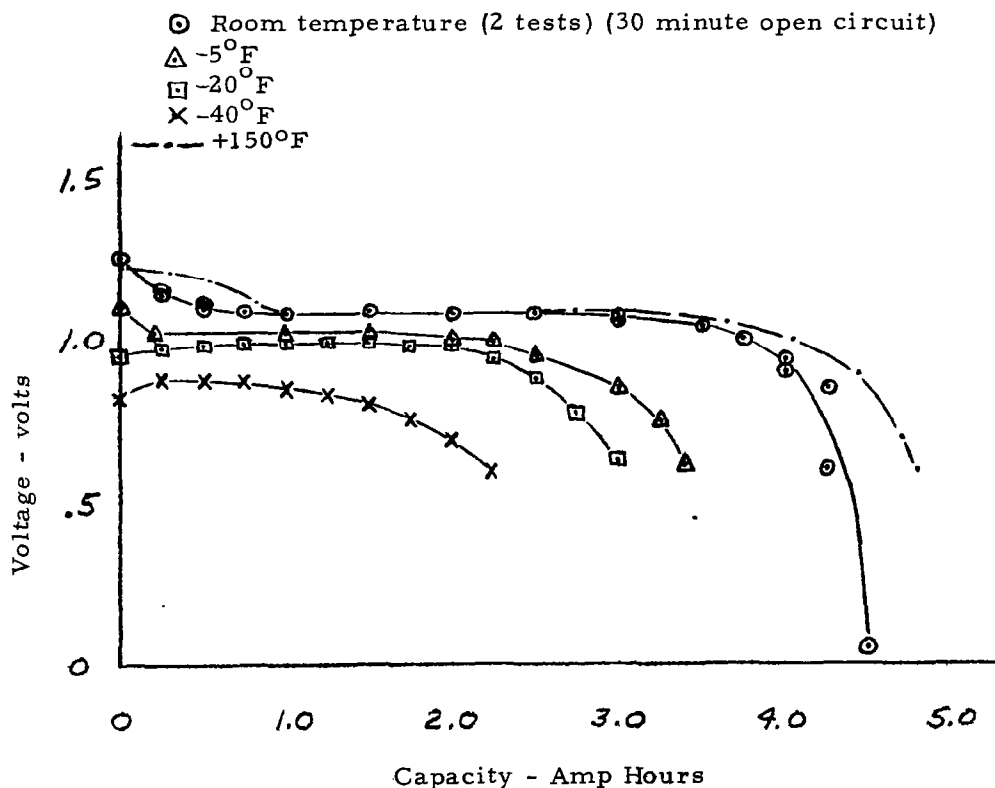


Figure 52

B. Battery Tests

Battery 1: Cycle record data are plotted in Figure 53, where voltages are shown:

- A - at the end of charge
- B - at the start of discharge
- C - at the end of discharge

as functions of the number of cycles completed. The cycle was 55 minutes at 17.6 volts constant potential charge/35 minutes at 3 ohms (4 ampere nominal) discharge. As early as the seventh cycle, electrolyte leakage was observed. The leakage became progressively worse, and the battery was removed at cycle 305 due to low capacity -- apparently due to loss of electrolyte. However, no electrolyte leakage was detected beyond the confines of the filament wound battery case.

Battery 2: It was suspected that the cause of failure of Battery 1 was due to lack of balance between the cells. This was verified with Battery 2, which was cycled without the filament wound battery case. This enabled the direct monitoring of individual cell voltages. Leakage was in evidence on the twelfth cycle, and the charge voltages across the battery are shown in Table XXXVIII.

Battery 3: The initial formed capacity of this battery was 3.2 ampere-hours (see Table XXXIV). After balancing, and before assembly, this cell group was jumper discharged in parallel at 0.4 ohm. Final assembly was done with the cells in the discharged condition. Activation of the battery, prior to the start of electrical cycling, was accomplished as follows:

1. First Cycle

Charge at 16.5 volts C. P., 0.25 A C. L. for 16 hours.
Discharge through six ohm resistance to 9.9 volts.

2. Second Cycle

Charge at 16.7 volts C. P., 0.50 A C. L. for 16 hours.
Discharge through six ohm resistance to 9.9 volts.

PERFORMANCE SUMMARY

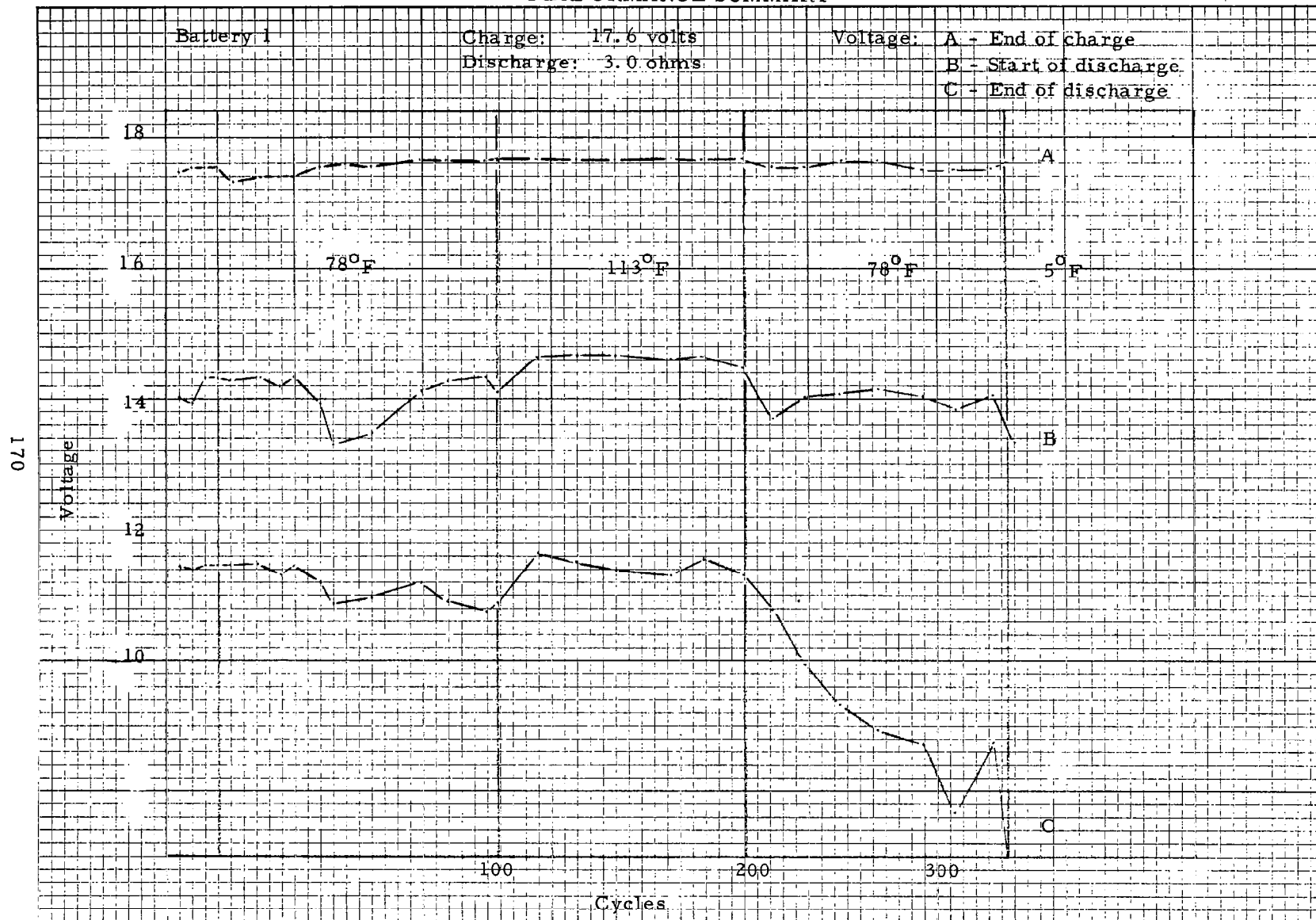


FIGURE 53

TABLE XXXVIII

CYCLE RECORD - BATTERY NUMBER 2

Room Temperature

Charge Time - 55 Minutes

Discharge Time - 35 Minutes

Resistance - 3.00 Ohms

<u>Cycle No.</u>	<u>Charge Cycles</u>		<u>Discharge Cycles</u>	
	<u>Start Volts</u>	<u>End Volts</u>	<u>Start Volts</u>	<u>End Volts</u>
1	-	17.60	14.70	11.60
2	13.44	17.60	14.72	11.66
3	13.44	17.60	14.68	11.60
4	13.44	17.62	14.66	11.58
5	13.44	17.62	14.58	11.54
6	13.44	17.62	14.66	11.54
7	13.42	17.62	14.64	11.42
8	13.52	17.62	14.66	11.46
9	13.54	17.62	14.58	11.42
10	13.48	17.64	14.58	11.52
11	13.48	17.64	14.58	11.52
12	13.58	17.64	14.58	11.42

Cell Voltages Across the Battery

<u>Cell No.</u>	<u>Voltage</u>
34	1.46
28	1.74
41	1.46
42	1.59
47	1.46
48	1.78
49	1.47
51	1.80
56	1.48
58	1.76
59	1.77

3. Third Cycle

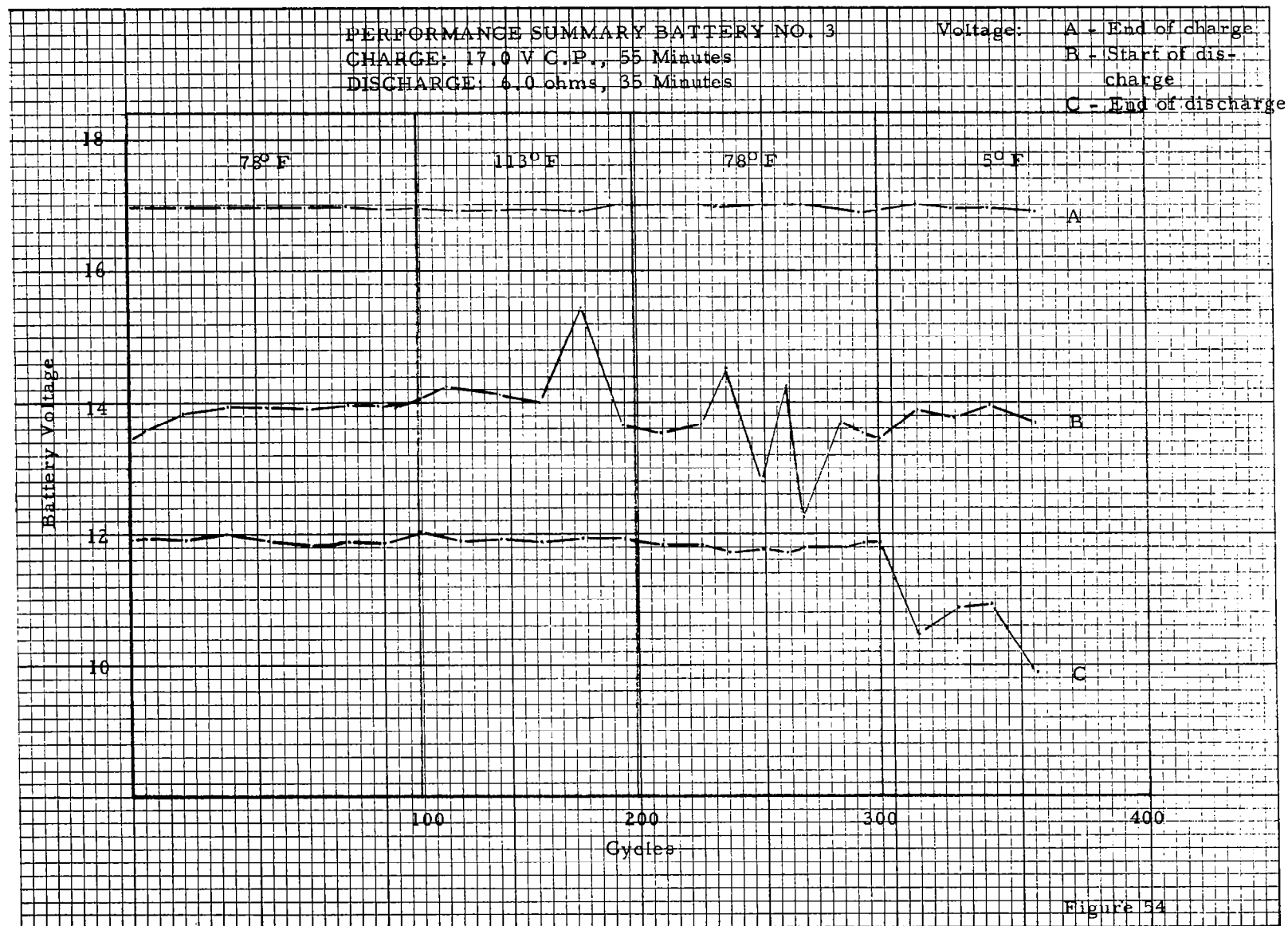
Charge at 17.0 volts C. P., 0.50 A C. L. for 16 hours. Start automatic cycling with six ohm discharge for 35 minutes.

4. Fourth Cycle

Charge at 17.0 volts C. P., 4 A C. L. for 55 minutes. Cycle through 25 total cycles. Stop cycling at the end of 26th charge. Finish charging at 17.0 volts C. P. overnight.

At this point, Battery 3 was put on cycling at 55 minutes, 17.0 volts constant potential charge/35 minutes, 6 ohms (2 ampere nominal) discharge. The battery was removed from cycling at the end of discharge number 357 (5⁰F) because of the conclusion of the program. At this time, a capacity determination was made by charging at 17.0 volts constant potential with a 4.0 ampere current limit for 16 hours, followed by a 2.0 ampere constant current discharge to 6.6 volts (0.60 volt per cell). The capacity to 0.60 volt per cell was 5.0 ampere-hours, and was 4.43 ampere-hours to 0.90 volt per cell. There was no electrolyte leakage observed, and it is assumed that the cells remained fairly well balanced. The performance summary of Battery 3 is presented in Figure 54.

The remaining batteries were activated, but were not placed on test due to the completion of the program.



XI. SUMMARY AND CONCLUSIONS - PHASE III

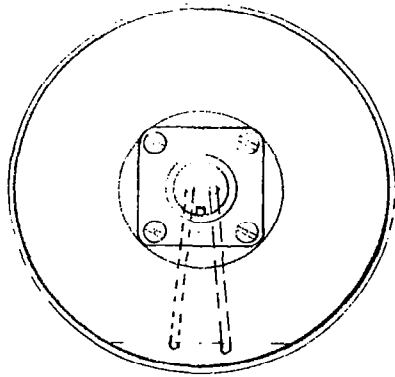
All of the original performance objectives of this program have been accomplished. The intended cell capacity of 200 ampere-minutes was the minimum qualification requirement for the cells at formation. Cycled cells and batteries exhibit capacities 50% in excess of the requirement. The temperature range over which the design has been evaluated has been exceeded by a good margin -- minus 40°F to 150°F, compared to the original goal of plus 32°F to 122°F. The weight, volume, and permeability values are all less than the original design goals.

The negative cadmium plate, made by the pasting procedure, has proved to be reliable. It is undoubtedly disadvantageous that formation requires a number of cycles. This presents quite an area for future study, e. g., individual plate formation as opposed to formation at the cell level; the design of proper cycling equipment; and instrumentation, as examples. This electrode construction should also be studied to determine the effect of extenders.

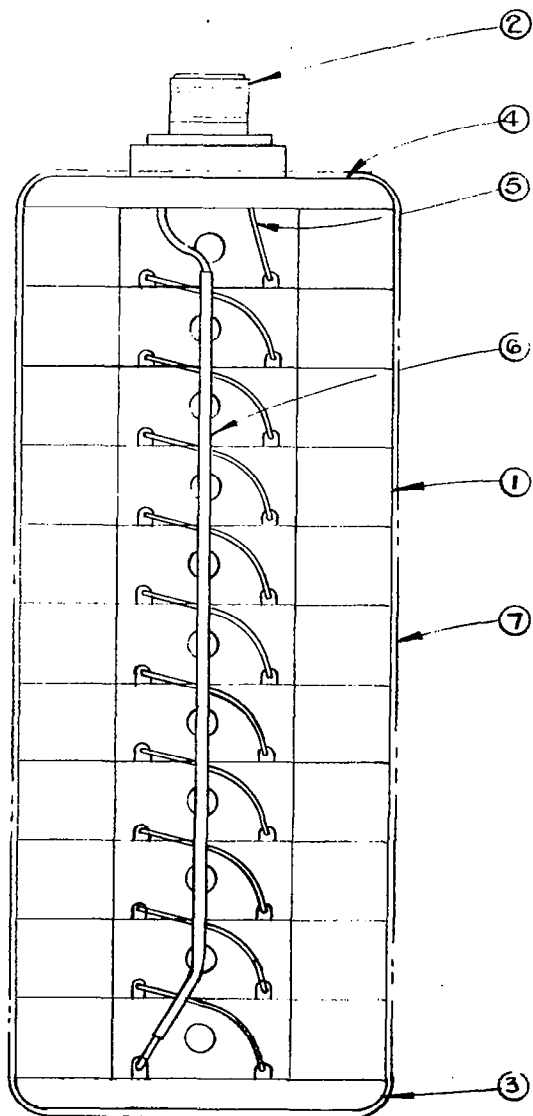
From a manufacturing point of view, more uniformity of the Permion 600 will be required before it can be considered for utilization in production batteries.

It is specifically recommended that a program intended to provide detailed manufacturing know-how in the production of highly reliable silver-cadmium batteries and cells specifically suited for the requirements of NASA should be continued. The results obtained would advance the state-of-the-art in the production of silver-cadmium batteries, and would enable the supply of hardware at minimum cost.

Figure 55. Battery Assembly

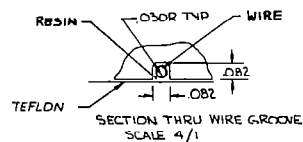
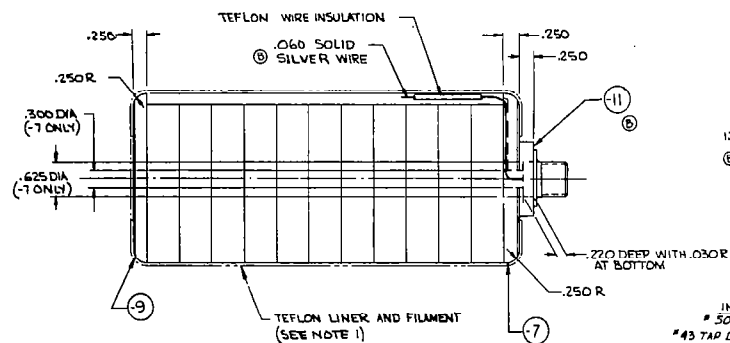
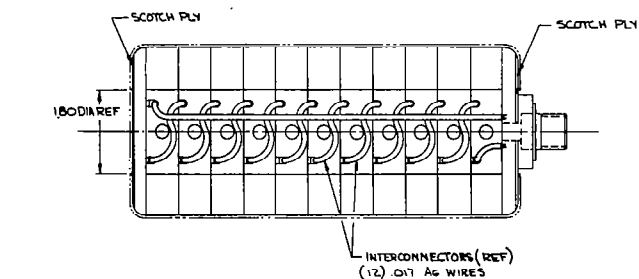


ITEM	REQD	DESCRIPTION
1	11	201321 CELL ASSY
2	1	CONNECTOR
3	1	BLANK END CAP
4	1	CONNECTOR END CAP
5	1	TERMINAL WIRE
6	1	TERMINAL WIRE
7	1	FILAMENT WOUND CASE

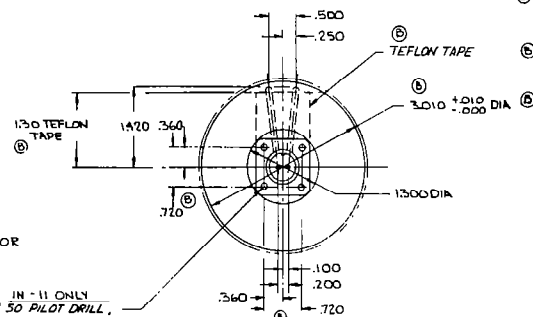


APPENDIX A

BATTERY TERMINAL ASSEMBLY



- IN -11 ONLY
 #50 PILOT DRILL
 #43 TAP DRILL THROUGH -11
 (8) .05K .025 DEEP PRIOR TO TAPPING
 TAP #4-40 THROUGH
 (TYP 4 PLACES)



- (7) TEFLON TAPE CAN BE OBTAINED FROM E.I. DUPONT DE NEMOURS CO. FILM DEPT INDUSTRIAL SALES 4455 FRUITLAND AVE LOS ANGELES, 58, CALIFORNIA
- (6) ISOTROPIC WENVE SCOTCHPLY 100Z CAN BE OBTAINED FROM MINNESOTA MINING & MFG CO. REINFORCED PLASTICS DIVISION, 600 BUSH AVE., ST PAUL MINNESOTA
- (5) E GLASS FLAKES CAN BE OBTAINED FROM OWENS CORNING FIBERGLASS, TOLEDO, OHIO

- (4) 1174/3 RESIN CAN BE OBTAINED FROM NARMCO MATERIALS DIVISION, A DIVISION OF TELECOMPUTING 600 VICTORIA AVENUE, COSTA MESA, CALIFORNIA
- (3) REMOVE ALL HIGH SPOTS AND STEPS PRIOR TO WINDING SO AS TO PRESENT A SMOOTH AND CONTINUOUS SURFACE.

1. ALL FILAMENT WINDING TO BE TO SPEC N° NRPS 1104 "FABRICATION OF BATTERY CASE"

NOTES

Figure 21. Battery Terminal Assembly



APPENDIX B

NARMCO PROCESS SPECIFICATION NRPS-1104B

NARMCO RESEARCH & DEVELOPMENT
A Division of Telecomputing Corporation
3540 Aero Court
San Diego 23, California

Spec. No. NRPS-1104B
Page 1 of 4

TITLE: Fabrication of Battery Case (NAS 5-1431)

PREPARED BY: R. A. Elkin

Approved by: 

DATE OF ISSUE: 18 March 1963

Approved by: 

This revised specification supersedes and replaces all previous issues of specification NRPS-1104.

The following procedures shall be followed in the fabrication of the NASA Battery Case (Contract No. NAS 5-1431) after the assembly of the cells, end plates, and wiring are received from Power Sources Division of Telecomputing Corporation.

1.0 MANDREL INSPECTION

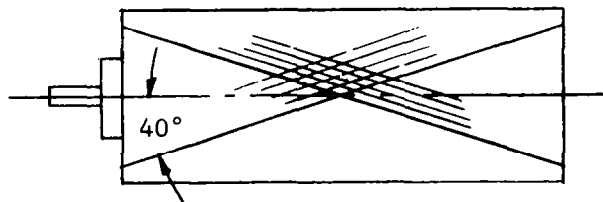
- 1.1 Upon receipt from Power Sources, the mandrel (cells, end plates, and wiring assembly) shall be visually inspected. A "soapy" feeling on the mandrel surface will be an indication of leakage of the electrolyte from one or more cells, and the Narmco project officer will be notified immediately.
- 1.2 Any spaces between cells, or cracks in cells, shall be brought to the attention of the project officer. If the project officer deems it advisable, the mandrel will be repaired with Quickset Dental Acrylic.
- 1.3 Any rough spots on the mandrel surface shall be lightly filed. Due care will be taken not to damage the cell walls during this procedure.
- 1.4 The mandrel shall be weighed to the nearest 0.1 grams and this weight recorded.
- 1.5 The mandrel diameter shall be measured at three points.
- 1.6 The mandrel length between end plates shall be measured.

2.0 GLASS CLOTH INTERLAYER

- 2.1 The mandrel will be lightly sanded with 600W sandpaper, washed with isopropanol, and allowed to air dry for several minutes.
- 2.2 One layer of 181 style glass cloth, impregnated with Quickset Dental Acrylic, shall be wrapped on the mandrel.
- 2.3 This will be over-wrapped with 5-mil mylar tape to apply pressure during the cure of 30 minutes at 100°F.
- 2.4 After cure, the surface shall be ground so that the glass is exposed.
- 2.5 If the mandrel surface is irregular enough to cause step 2.4 to expose the styrene cell container surface at any point, steps 2.2, 2.3 and 2.4 shall be repeated - except that 108 style cloth shall be used in place of the 181 cloth.

3.0 WINDING SETUP

- 3.1 The helical winding machine shall be adjusted to a rotational speed of 56 RPM.
- 3.2 The traverse mechanism shall be adjusted to obtain a counter reading of 28 cycles per minute where one cycle is a movement of the fiber guide across and back.
- 3.3 The mandrel will be placed in the machine and dry, single-end glass roving run through the fiber guide and attached to one end of the mandrel.
- 3.4 The machine will be turned on and adjusted to obtain a leading pattern with a winding angle of approximately 40°. Fiber tension per one end is 0.25 lbs.



- 3.5 The counter will be zeroed and one complete layer of dry roving wound on the mandrel.

3.6 At the completion of step 3.5, the counter should read between 150 and 180. If it does not, an adjustment of the traverse speed will be made and steps 3.5 and 3.6 repeated.

3.7 The lead screw speed shall be set for 0.0166 in/rev. This is a gear setting of C-6 on Narmco's machine.

4.0 TEFLON IMPERMEABILITY LAYER

4.1 A thin (.005" to .010") coat of 80 parts Epon 820 and 20 parts Lancaster "A" shall be applied to the mandrel.

4.2 A small spot on one end plate will be cleaned with GA-1B neutralizer and two or three drops of Eastman 910 adhesive applied to this spot.

4.3 The end of a roll of DuPont FEP Teflon tape will be anchored on with the Eastman 910. This tape shall be 1" wide by 0.002" thick, and the type which has been treated to make it bondable on both sides.

4.4 Two layers of tape will be wrapped circumferentially around the mandrel, and overlapping itself approximately 1/4" to 3/8". While wrapping the tape, it shall be slightly tensioned (approximately 1/4 lb) and resin (80/20 - Epon 820/Lancaster "A") shall be applied to its outside surface.

4.5 The end of the tape shall be anchored to itself with Eastman 910 adhesive.

4.6 Two layers of circumferentially wound tape, 1" wide, shall be wound at both ends of the battery, using Eastman 910 adhesive for anchoring and 80/20 - Epon 820/Lancaster "A" resin for bonding.

4.7 Two layers of single-end HTS glass roving, impregnated with 50/50 - Epon 820/Lancaster "A" and tensioned to 0.25 lb, shall be wound circumferentially over the tape for the width of one inch at each end. The lead screw setting of C-6 on Narmco's machine shall be used for this. One layer of roving shall be wound over the remainder of the battery.

4.8 If the tape protrudes past the edge of the end plate at either end, it shall be trimmed with a pair of scissors.

5.0 WINDING OF THE BATTERY SHELL

5.1 The resin system for the windings shall be 50/50 - Epon 820/Lancaster "A", and the tension shall be 0.25 lb per end.

- 5.2 The counter shall be zeroed and helical windings applied to the battery case.
- 5.3 At the completion of one layer of helical windings, the counter reading shall be noted. The total number of layers to be applied is dependent upon the counter reading:

<u>Counter Reading for 1 Layer</u>	<u>No. of Layers Required</u>
125 to 166	4
167 to 220	3

- 5.4 At the completion of the helical windings, the total counter reading and number of layers shall be recorded.
- 5.5 Circumferential fibers will be wound to a thickness of one layer, except at each end where two layers will be wound for the width of one cell. The lead screw speed shall be 0.0166 in/rev. and fiber tension 0.25 lb/end.
- 5.6 After winding, excess resin will be wiped off, or extra resin added, to obtain a uniform thin resin coverage over the battery,
- 5.7 The battery will be cured at least eight hours at room temperature. During the first four hours, or until the resin is too tacky to flow, the battery will be slowly rotated (approximately 10 RPM).
- 5.8 The completed battery shall be post cured in an oven for fourteen hours at 125°F.

APPENDIX C

PRELIMINARY PROTOTYPE BATTERY SPECIFICATION

POWER SOURCES DIVISION
TELECOMPUTING CORP.
DENVER, COLORADO

No. 60043
May 15, 1963

PRELIMINARY PROTOTYPE BATTERY SPECIFICATION

1. SCOPE

This specification covers the requirements for sealed silver-cadmium batteries of a 12 nominal voltage and a 4.0 ampere-hour nominal capacity.

2. APPLICABLE DOCUMENTS

The following documents of the issue in effect of invitations for bids, form a part of this specification.

Specifications

Military

Mil-E-5272C, Environmental Testing,
Aeronautical and Associated Equipment,
General Specification for

Drawings

4 AH Sealed Cell, Power Sources Division
of Telecomputing Corporation (Figure 38)

Battery Assembly, Power Sources Division
of Telecomputing Corporation (Figure 55)

3. REQUIREMENTS

3.1 MECHANICAL DESIGN

3.1.1 Number of Cells

The battery shall consist of eleven (11) cells connected in series.

- 3.1.1.1 The dimensions of each cell shall conform to the drawing shown in Figure 38.
- 3.1.1.2 The weight of each cell shall be 0.3 pound.
- 3.1.1.3 Cell cases, covers and plugs shall be of styrene-acrylonitrile copolymer material, ASTM D 1431-56T. The use of other materials shall be subject to prior approval.
- 3.1.1.4 The cells shall be vacuum sealed to three psia using a mixture of nitrogen and helium gases.
- 3.1.2 Thermal - The thermal design shall be such that the cells will operate within the limits specified in 3.3.3.
- 3.1.3 Mechanical - The battery configuration shall be cylindrical, and shall be mounted in such a manner that motion will be restricted in all directions.

The mounts shall not impose stresses on the battery from relative motion of the mounts. The battery structure shall withstand dynamic forces as follows:

- 3.1.3.1 Vibration - The battery shall be cycled from 5 to 3000 cps and back to 5 cps in a period of nine (9) minutes at an acceleration of ± 20 g with a double amplitude of 0.4 inch. Crossover shall be at 31 cps. The battery shall be vibrated in the above manner along each of three mutually perpendicular axes. The rate of frequency change shall be logarithmic.
- 3.1.3.2 Acceleration - In accordance with Procedure III of Mil-E-5272C (ASG), except that 20 g shall be used in lieu of 14 g.
- 3.1.3.3 Shock - In accordance with 4.15.5.1 of Mil-E-5272C (ASG), except that 40 g shall be used in lieu of 15 g.
- 3.1.4 Weight - The battery assembly shall be made as light as is compatible with good design practice, but shall not exceed 3.6 pounds.
- 3.1.5 Volume - The battery volume shall be maintained at the minimum possible to contain the cells and necessary battery components, but shall not exceed 55 cubic inches, excluding the connector.

3.1.6 Materials - The materials used for battery assembly shall be those shown in the attached assembly drawing.

3.2 ELECTRICAL DESIGN

3.2.1 Capacity - The battery shall have a minimum capacity of four ampere-hours when discharged at the five-hour rate to 6.6 volts.

3.2.2 Discharge - The battery shall be capable of a four ampere discharge for 35 minutes at a voltage of 12 volts plus 2.5 volts minus 1.0 volt.

3.2.3 Charge - The battery shall be capable of a 17 volt constant potential charge for 55 minutes to satisfy the requirements of 3.2.2.

3.3 PERFORMANCE

3.3.1 Operation Position - The battery shall be capable of operating in any position.

3.3.2 Vacuum Operation - The battery shall be capable of operating in a vacuum of 10^{-2} mm Hg.

3.3.3 Operating Temperature - The battery shall be capable of operating between -20°F as a lower limit and 120°F as an upper limit.

3.3.4 Life - The battery shall have a mean cycle life of 1000 cycles of the type specified in 3.2.2 and 3.2.3 over the temperature range specified in 3.3.3.

4. QUALITY ASSURANCE PROVISIONS

4.1 CLASSIFICATION OF TESTS

The inspection and testing of batteries shall be classified as follows:

- a. Qualification Tests
- b. Acceptance Tests

- 4.1.1 Qualification Tests - Qualification tests shall be conducted on randomly chosen cells. Such tests shall consist of:
- a. Performance Tests
 - b. Environmental Tests
- 4.1.1.1 Performance Tests - Performance tests shall be conducted on randomly chosen cells to demonstrate that the cells meet the electrical performance requirements specified in 3.2.
- 4.1.1.2 Environmental Tests - Environmental tests shall be conducted on randomly chosen cells to demonstrate that the cells meet the requirements of 3.1.3.
- 4.1.2 Acceptance Tests - Acceptance tests shall be conducted on each production unit. Such tests shall consist of:
- a. Capacity Check
 - b. Inspection
- 4.1.2.1 Capacity Check - A capacity check shall be made by first charging in accordance with paragraph 3.2.3 until the current becomes less than 50 milliamperes, then discharging to 0.6 volt per cell at four amperes constant current. The battery shall deliver a minimum of four ampere hours to the specified cut-off voltage.
- 4.1.2.2 Inspection - Each battery shall be inspected for the purpose of demonstrating that it was manufactured in accordance with high-grade battery manufacturing practice.

5. MARKING

5.1 INFORMATION REQUIRED

Each cell case shall be marked with the following information:

Name of Manufacturer
Model Number
Serial Number
Location of Positive Terminal

6. PREPARATION FOR DELIVERY

6.1 PACKING AND SHIPPING

Packing and shipping shall be done in accordance with standard commercial practice.

7. NOTES

7.1 INTENDED USE

The rechargeable silver-cadmium battery is used to furnish power for stabilization of all loads during the dark period and periods of peak power requirements.

APPENDIX D

POWER SOURCES TEST PROCEDURE NUMBER 60219

1.0 REFERENCES

- 1.1 Cook Battery Company Proposal Number 483A.
- 1.2 Mil-E-5272C (ASG) Environmental Testing.
- 1.3 NASA Contract Number NAS5-1431.

2.0 SCOPE

This specification covers the methods and conditions which govern the electrical and environmental testing of batteries manufactured under the referenced contract.

3.0 NUMBER OF BATTERIES TO BE TESTED

- 3.1 Two groups of four batteries (eight (8) batteries total), shall be tested to determine compliance with the requirements specified herein.
 - 3.1.1 Three batteries from each group shall be cycled according to the requirements of Paragraphs 5.0 through 5.4 of this specification.
 - 3.1.2 One battery from each group shall be subjected to the environmental tests outlined under Paragraphs 6.0 through 6.7.2 of this specification.

4.0 TEST CONDITIONS

- 4.1 All tests shall be conducted at local atmospheric pressure, room (ambient) temperature, relative humidity 90% or less, and in a vertical position (Z_1 axis up), unless otherwise specified.
- 4.2 Each battery specified in Paragraph 3.1.2 shall be potted (ends only) in a 3.5 inch O.D., 11 gauge, 8.5 inch long steel tube with a rigid material.
 - 4.2.1 Prior to potting, the battery shall be covered with one layer of Scotch tape to prevent adherence of the potting material to the battery casing.

- 4.3 Any evidence of a change which in any manner prevents the battery from meeting functional, maintenance or other requirements of service life shall be a criterion for considering the specimen to have failed. Criteria for failure shall be those expressed in Paragraphs 7.0 through 7.4.

5.0 ELECTRICAL AND TEMPERATURE TEST OF SIX BATTERIES

- 5.1 The temperature-electrical cycle test regime shall be as follows:

- 5.1.1 Twenty-five conditioning cycles at rates and times determined by the Project Engineer shall be applied at room temperature prior to the tests described in subsequent paragraphs.

5.1.2	Temperature (°F)	Number of cycles	Cycle Time (min.)		Cumulative Cycles
			Charge	Discharge	
	78	96	55	35	121
		1	1405	35	122
	113	96	55	35	218
		1	1405	35	219
	78	96	55	35	315
		1	1405	35	316
	5	96	55	35	412
		1	1405	35	413

- 5.1.3 Continued cycle testing shall be at room temperature and at the 55-minute charge - 35-minute discharge cycle unless otherwise specified by the Project Engineer.

- 5.2 Three batteries shall be tested per the schedule of Paragraph 5.1, with discharge to be made through 3 ohms fixed resistance (4.0 amperes nominal), and with charge to be applied at a current limited, constant potential of 17.6 volts (maximum) for a minimum of 413 cycles.

- 5.3 Three batteries shall be tested per the schedule of Paragraph 5.1, with discharge to be made through 6 ohms fixed resistance (2.0 amperes nominal), and with charge to be applied at a current limited, constant potential of 17.6 volts (maximum) for a minimum of 413 cycles.

6.0 ENVIRONMENTAL TESTS

6.1 One battery from each group (2 batteries total) shall be tested under the following environments and conditions:

6.1.1 A helium leak test, as specified in Paragraph 6.7, shall be conducted on the specimen (fully charged) prior to the position test (Paragraph 6.2), after the vacuum test (Paragraph 6.3), and after the shock test (Paragraph 6.6).

6.1.2 Prior to the start of the environmental tests, the specimen shall have completed a minimum of 100 charge-discharge cycles as specified in Paragraph 6.1.3.

6.1.3 The specimen shall be discharged through a fixed resistance of 3 ohms (2.0 amperes nominal) for 35 minutes and shall be charged at a current limited, constant potential of 17.6 volts (maximum) for 55 minutes.

6.1.4 After each environmental test, unless otherwise specified, the specimen shall be given a minimum of 16 cycles of electrical tests as specified in Paragraph 6.1.3 to check for any deterioration or change in performance which may be due to the environmental test.

6.2 Position Test

6.2.1 The specimen shall be electrically cycled as specified in Paragraph 6.1.3 for six hours in each of the following positions (Reference Figure 1):

Six hours (4 cycles) with Y_1 axis up.
Six hours (4 cycles) with X_1 axis up.
Six hours (4 cycles) with Z_2 axis up.

6.3 Vacuum Test

6.3.1 The specimen shall be subjected to a vacuum of at least 6.0×10^{-2} mm Hg for a minimum of 72 hours while functioning in accordance with Paragraph 6.1.3.

6.4 Vibration Test (Operative)

6.4.1 The potted specimen shall be attached to a rigid fixture capable of transmitting the vibration conditions specified herein.

- 6.4.2 The battery shall be charged at a constant potential of 17.6 volts until the current flow is less than 0.2 amperes, and shall be discharged through 6 ohms resistance (2.0 amperes nominal) to a minimum voltage equal to 8.8 volts.
- 6.4.3 Vibration tests shall be conducted during the discharge portion of the electrical function test only, as per Paragraph 6.4.2.
- 6.4.4 The amplitude of applied vibration shall be monitored on the test fixture near the specimen mounting points.
- 6.4.5 The specimen shall be cycled from 5 to 3000 cps and back to 5 cps in a period of 9 minutes at an acceleration of ± 20 g with a double amplitude of 0.4 inches. Crossover shall be at 31 cps. Specimen shall be vibrated in the above manner along each of three mutually perpendicular axes. The rate of frequency change shall be logarithmic.
- 6.5 Acceleration Test (Operative)
 - 6.5.1 The specimen shall be subjected to a steady acceleration of 20 g for one minute along each of its six directions (i.e., along both directions of its three mutually perpendicular axes) by a centrifuge (see Figure 1 for axial directions).
 - 6.5.1.1 The acceleration of 20 g applies to the geometric center of the specimen.
 - 6.5.2 The acceleration test shall be conducted during the discharge portion only of the electrical function test as specified in Paragraph 6.1.3. The discharge shall be started a minimum of one minute preceding acceleration and run continuously (except it is permissible to stop discharge for position change) through all acceleration plus five minutes after acceleration test.
- 6.6 Shock Test (Non-Operative)
 - 6.6.1 The specimen shall be in a charged condition.
 - 6.6.2 The specimen shall be subjected to 18 impact shocks of 40 g acceleration, each shock impulse having a time duration of 11 ± 1 milliseconds reaching maximum acceleration at approximately 5.5 milliseconds.

- 6.6.3 The intensity shall be within + 10% when measured with a filter having a band-width of $\bar{5}$ to 100 cycles per second.
- 6.6.4 The shocks shall be applied in the following directions:

Vertically, three shocks in each direction of the Z axis; parallel to the major horizontal axes, three shocks in each direction of the X axis; parallel to the minor horizontal axes, three shocks in each direction of the Y axis.
- 6.6.5 After the shock test is completed the battery shall be cycled according to Paragraph 6.1.3.
- 6.7 Helium Leak Test
 - 6.7.1 The unit shall be tested for leaks by a mass-spectrometer-type helium leak detector according to SPS 160A, which specifies that a 90 - 10 nitrogen - helium mixture be introduced into the specimen prior to sealing, and that a vacuum be pulled externally into the helium mass-spectrometer.
- 7.0 CRITERIA OF FAILURE
 - 7.1 A battery may be considered to have failed electrically when a voltage less than 6.6 volts is reached prior to the completion of 35 minutes of discharge.
 - 7.2 A battery may be considered to have failed structurally if there is noticeable leakage and/or rupture of the battery case.
 - 7.3 If a battery failure occurs due to the malfunction of the test equipment without any structural damage taking place, the battery may be cycled manually. If performance has not been adversely affected, the battery may be returned for testing.
 - 7.4 An analysis of each failed battery shall be made by the Project Engineer and recorded on the failure analysis form that is attached herein.

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8.0 MAXIMUM ALLOWABLE TOLERANCES ON TEST CONDITIONS
AND EQUIPMENT

The maximum allowable tolerances on test conditions and
equipment shall be as follows:

Temperature:	$\pm 2^{\circ}\text{C}$ (exclusive of accuracy of instruments)
Vibration Amplitude:	$\pm 10\%$
Vibration Frequency:	$\pm 2\%$
Acceleration Force.	$\pm 10\%$
Shock Force:	$\pm 10\%$
Vacuum Pressure:	$\pm 10\%$
Voltage Regulation:	$\pm 1\%$
Current Resistance.	$\pm 1\%$
Time:	± 15 seconds

9.0 DATA COLLECTION

9.1 Life cycle, position and vacuum tests, Paragraph 5.0, 6.2 and
6.3.

9.1.1 Each battery voltage shall be monitored and recorded at
least once every two minutes.

9.1.2 Discharge resistances for each battery shall be recorded
twice each working day.

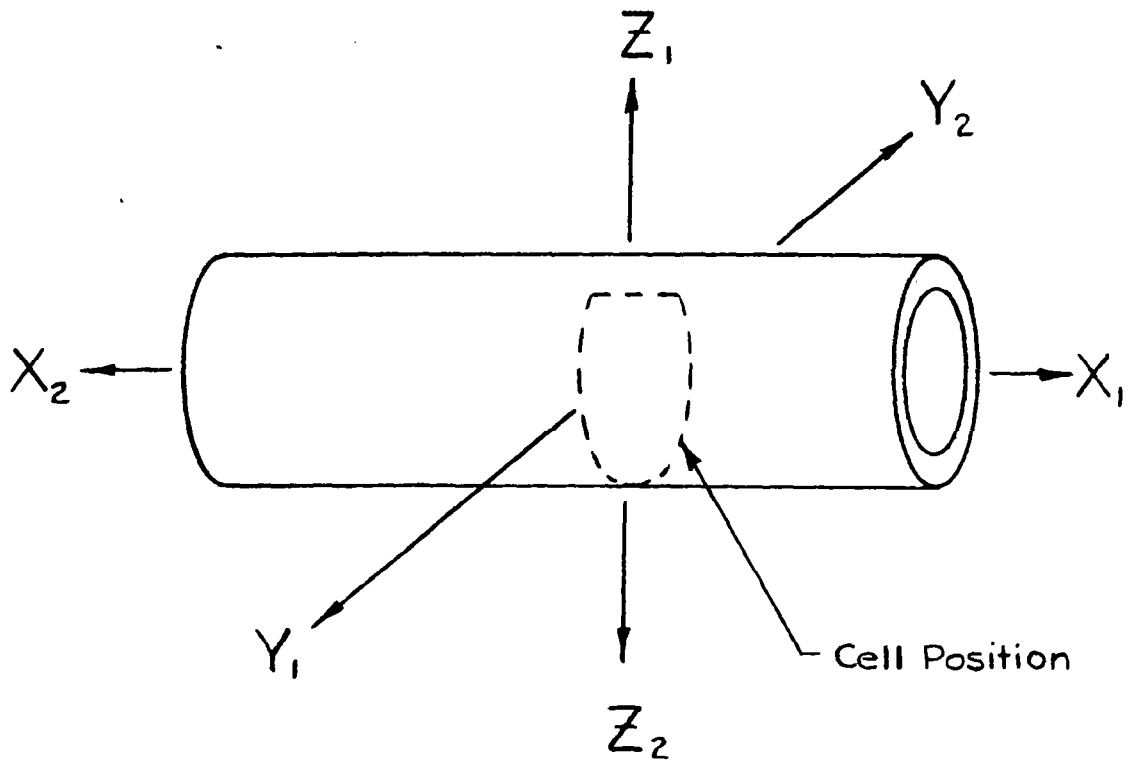
9.1.3 Test progress and charges shall be recorded on the cycle
record sheets.

9.2 Operating Vibration Test

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- 9.2.1 Voltage monitoring and recording of each battery shall be continuous on a chart at a speed of not less than three inches per minute, and recorded as designated on Cycling Record.
- 9.3 Acceleration
- 9.3.1 Voltage and current monitoring and recording of each battery shall be continuous on a chart at a speed of not less than 12 inches per minute, and recorded as designated on Cycling Record.
- 9.4 Leak Rate
- 9.4.1 The leak rate shall be recorded prior to the position test (Paragraph 6.2), after the vacuum test (Paragraph 6.3, and after the shock test (Paragraph 6.6).

FIGURE 1



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ENVIRONMENTAL TEST RESULTS

Vibration (Operative), Paragraph 6.4

		<u>X Axis</u>	<u>Y Axis</u>	<u>Z Axis</u>
Date	Mo., Day, Yr.			
Battery	No.			
Cycle	No.			
Temperature	°F			

Model and Serial
Numbers of
Instruments Used:

Test Remarks _____

Tested by _____ Title _____

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ENVIRONMENTAL TEST RESULTS

Acceleration (Operative), Paragraph 6.5

<u>Reading</u>	<u>Units</u>	<u>X Axis</u>	<u>Y Axis</u>	<u>Z Axis</u>
		Fwd/Rvs	Fwd/Rvs	Fwd/Rvs
Date	Mo., Day, Yr.			
Battery	No.			
Cycle	No.			
Temperature	°F			
Centrifuge Arm	In.			
Rotation Speed	Revs. /min.			
Acceleration	g			
Model and Serial Numbers of Instruments Used				

Test Remarks: _____

Tested by: _____ Title: _____

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ENVIRONMENTAL TEST RESULTS

Shock (Non-Operative), Paragraph 6.6

<u>Reading</u>	<u>Units</u>	<u>X Axis</u> Fwd/Rvs	<u>Y Axis</u> Fwd/Rvs	<u>Z Axis</u> Fwd/Rvs
Date	Mo., Day, Yr.			
Battery	No.			
Cycle	No.			
Temperature	°F			
Shock Impulse	Shock No.			
Duration	1 - Msec			
	2 - Msec.			
	3 - Msec.			
Maximum	Shock No.			
Impact	1 - g			
Acceleration	2 - g			
	3 - g			
Acceleration	Shock No.			
Reached at	1 - g			
5.5 Msec.	2 - g			
	3 - g			

Model and Serial
Numbers of
Instruments Used

Test Remarks: _____

Tested by: _____ Title: _____

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BATTERY FAILURE ANALYSIS

Environmental Test _____ Paragraph _____

Battery No. _____ Cycle No. _____ Temperature _____ °F

Charge

Discharge

Time _____ min.

Time _____ min.

Constant Potential _____ volts

Resistance _____ ohms

Nominal Current _____ amperes

Date of Failure _____

Criteria for Terminating Test _____

Visual Inspection (battery)

Remarks

Case Leakage

Case Distortion

Seal Leakage

Excessive Heat

Visual Inspection (cells)*

Position Number (pos. to neg.) 1 2 3 4 5 6 7 8 9 10 11

Mfg. Number

Case Leakage

Case Distortion

Seal Leakage

Excessive Heat

* (✓ - Good: X - Damaged)

Signature _____ Title _____ Date _____

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CELL AUTOPSY

Battery No. _____ Cell No. _____
Terminals _____
Tabs _____
Negatives _____
Positives _____
Separation _____
Electrolyte _____
Case _____

Separator Ag Content (mg/layer)	No. 1 _____	No. 5 _____
	No. 2 _____	No. 6 _____
	No. 3 _____	No. 7 _____
	No. 4 _____	

Remarks _____

Signature: _____ Title: _____ Date: _____

Battery No. _____ Cell No. _____
Terminals _____
Tabs _____
Negatives _____
Positives _____
Separation _____
Electrolyte _____
Case _____

Separator Ag Content (mg/layer)	No. 1 _____	No. 5 _____
	No. 2 _____	No. 6 _____
	No. 3 _____	No. 7 _____
	No. 4 _____	

Remarks _____

Signature: _____ Title: _____ Date: _____

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Leak Rates

cc/sec.

Prior to Position Test (Para. 6.2)

Remarks: _____

Signature: _____

Title: _____

Date: _____

Following Vacuum Test (Para. 6.3)

Remarks: _____

Signature: _____

Title: _____

Date: _____

Following Shock Test (Para. 6.6)

Remarks _____

Signature: _____

Title. _____

Date: _____

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60219

SHEET 4

BATTERY

211

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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